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Evaluation of Radiolysis Data for Hydrogen Gas Generation During Gamma Irradiation of Pre-Corroded and Pristine Aluminum Samples – An Aluminum SNF Dry Storage Study Interim Report

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ASNF	Aluminum-Clad Spent Nuclear Fuel
CY20	Calendar Year 2020
DOE	Department of Energy
EDS	Energy Dispersive Spectroscopy
EM	Environmental Management
GC	Gas Chromatograph
Gy	Gray [1 Gy = 100 Rad = 1 Joule per Kg = 6.2415×10^{12} MeV per Kg]
INL	Idaho National Laboratory
kGy	kiloGray
NE	Nuclear Energy
RH	Relative Humidity
SEM	Scanning Electron Microscopy
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
TCD	Thermal Conductivity Detector
TD	Technology Development
XRD	X-ray Diffraction

1.0 Summary

Information and data from radiolysis testing to measure hydrogen (H_2) generated from hydrated oxides on aluminum exposed to ^{60}Co radiation were reviewed to evaluate hydrogen generation with radiation dose. Hydrogen generation rate is a primary input to the coupled thermal-chemical system model of the performance of aluminum-clad spent nuclear fuel in a dry storage canister (ASNF-in-canister) over its storage life.

Hydrogen generation data and hydrogen generation rate (hydrogen generated per absorbed radiation dose, $\Delta(H_2)/\Delta(\text{dose})$) were reported in two reports for radiolysis testing [1, 2]. The testing involved first-time data[1] for radiolytic yield of hydrogen from hydrated-oxides-on-aluminum substrates, and from pristine (non-corroded) aluminum substrates. The laboratory-grown hydrated-oxides-on-aluminum substrates contained a ~ 5 μm film consisting of the trihydroxide bayerite ($Al(OH)_3$) with amounts of the oxyhydroxide boehmite (AlOOH). These specimens were assumed to also contain physisorbed water (unquantified). The pristine substrates were flat coupons of aluminum that were ground to a 600-grit finish but were not immersed in water to grow a hydrated oxide. The pristine substrates were tested as companion specimens to provide information on hydrogen generation from material without chemisorbed water and were assumed to contain physisorbed water (unquantified).

The test parameters for the ^{60}Co irradiation included:

- Cover gas: Air; Nitrogen (N_2); Argon (Ar)
- Target relative humidity (RH) in the test vessel (ampule): 0; 50; 100%
- Irradiation dose[2] (calculated to be deposited in the entire sample volume, including the oxide and aluminum substrate): 240 to 1104 kGy
- Irradiation temperature: ambient cell temperature (assumed to be slightly elevated from room temperature); 100°C; 200°C

Figure 1 below shows the hypothesized phenomenological response of a system of hydrated-oxides-on-aluminum with physisorbed water under a cover gas in a closed chemical system to absorbed gamma dose. Several regimes of H_2 generation are hypothesized for the N_2 and Ar cover gas conditions:

- A transient regime (dose of 0 to approximately 500 kGy) in which the H_2 generation rate is non-linear and the primary source of $H_2$is from physisorbed water
- A regime with a constant H_2 generation rate similar for both Ar and N_2 cover gases with physisorbed water as the primary source of the H_2
- A regime with a constant H_2 generation rate similar for both Ar and N_2 cover gases with

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[1] The test specimen design involved coupons of aluminum 1100 onto which a film of hydrated oxides was grown, and coupons that were tested in a pristine condition (without a hydrated oxide film), to determine the stable radiolytic hydrogen gas produced from them under ^{60}Co irradiation. There is no consensus test standard (e.g. ASTM International) for radiolysis testing of materials. In addition, there is no analytic model available to predict radiolytic gas generation rates from solid hydrated oxides. The test methods and approach used to develop hydrogen generation data from hydrated-oxides-on-aluminum substrates was the judgment of the INL/SRNL expert team.

[2] The hydrogen generation rate is typically reported as the "G_{H2}-value," the molecules of H_2 per 100 eV of energy deposited into the material. Evaluation of the G-value for hydrated-oxides-on-aluminum is subject to different constructions – energy deposited and contributing to the yield could be assumed to be just from the oxide, or it could include energy deposition into the aluminum substrate too. Further, for physisorbed water at (assumed) monolayer levels, energy deposition is also subject to different constructions. For purposes of this report, the energy deposited into the entire hydrated-oxide-on-substrate specimen is used to evaluate radiolytic H_2 yield from the specimen. The hydrogen generation rates from film-only energy deposition and from bulk deposition are reported in reference 1.

chemisorbed water as the primary source of the H_2. This regime does not appear to have been reached in the testing to date. This regime would span over a long dose interval over which the chemisorbed water from a thick hydrated oxide is being slowly consumed. The hydrogen concentration would saturate with full depletion of this water, or if chemical equilibrium with back reactions would be achieved.

In this present report, the data at dose levels greater than ~ 500 kGy from the full data set of this testing [1, 2] were considered to provide insights as to the likely origin (physisorbed vs chemisorbed water) of the H_2 radiolytic yield. Hydrogen generation (µL at standard temperature and pressure conditions) vs. absorbed dose (kGy) was plotted and hydrogen generation rate data (µL kGy^{-1}) was determined.

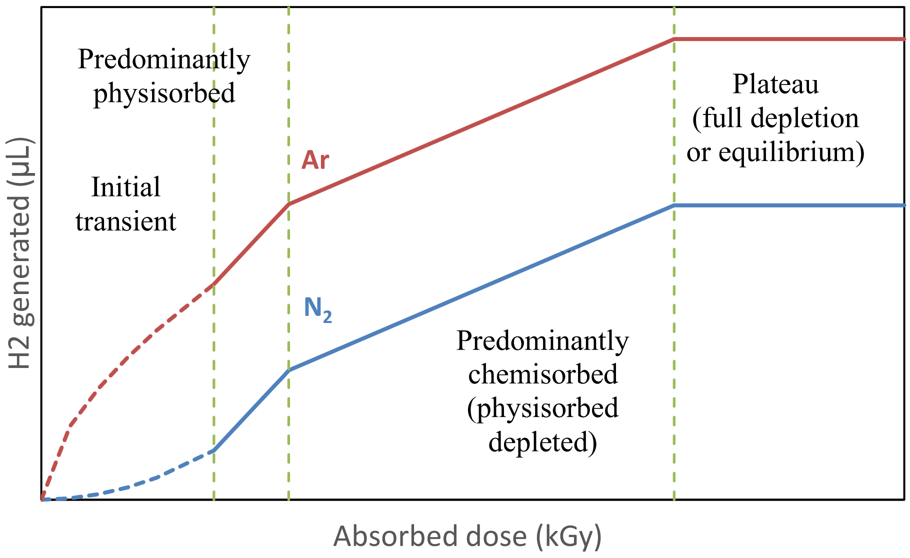

Figure 1. Hypothesized yield of hydrogen from hydrated oxides on aluminum under a cover gas

The findings and preliminary conclusions:

- Oxygen in the cover gas suppresses hydrogen generation [1]. (Further testing with oxygen is not pursued.)
- Hydrogen generation rate is independent of cover gas (N_2 and Ar) following an initial transient period (< 500 kGy dose) in which the H_2 yield and generation rate from N_2 was less than Ar [1, Figure 7]. The cause of this transient was assumed to be the radiolytic production of NH_x that effectively suppressed H_2. No further NH_x generation was assumed to occur after an equilibrium with NH_x is established.
- Physisorbed water is the primary contributor to the hydrogen generation rate in a material system of physisorbed and chemisorbed waters on aluminum over the dose range tested. (Depletion of the physisorbed water would occur with additional dose, and chemisorbed water/hydroxyls would be the sole contributor to hydrogen generation thereafter.)
- It is hypothesized that the radiolytic gas generation from hydrated-oxides-on-aluminum with physisorbed water with dose can be separated into several regimes including; 1) an initial region with varying H_2 generation rate dependent on cover gas, 2) a regime with a constant generation rate of H_2 primarily from radiolysis of water vapor and physisorbed water, 3) a regime with a constant (steady-state) radiolytic gas generation rate of H_2 primarily from the radiolysis of

chemisorbed water. This rate would continue until the hydrogen from the chemisorbed water is exhausted or an equilibrium is established with back reactions.

Additional radiolysis testing in calendar year 2020 (CY20) is being planned to allow better discrimination of physisorbed vs. chemisorbed contributions to H_2 yield and the dose regimes over which they dominate. Data for thermally-conditioned ("dried") hydrated oxides will also be developed. The completion of the CY20 testing will lead to identification of the "steady-state" H_2 generation rates that would be input to the ASNF-in-canister performance model to provide the best estimate of the evolution of gas composition over decades of dry storage.

2.0 Introduction

Preliminary data on radiolytic yields of molecular hydrogen (H_2) from ("pre-corroded") hydrated-oxides-on-aluminum substrates and from pristine aluminum substrates has been generated in Task 2 [1, 2] for the technology development program to enable safe extended dry storage of aluminum-clad spent nuclear fuel (ASNF) [3]. This present report further evaluates that preliminary data to provide insight into the origin of the observed radiolytic H_2. The sources of H_2 are assumed to be radiolysis of physisorbed and/or chemisorbed waters on the aluminum specimens – that is, the analysis assumes no contribution to H_2 generation due to corrosion of aluminum with free water

This evaluation provides insights on radiolytic H_2 generation to enable informed follow-on testing and selection of inputs for an ASNF-in-canister performance model developed under Task 3.

3.0 Supporting Information

3.1 Experimental Parameter Summary

Two sets of radiolytic data were generated and reported in references 1 and 2.

In both references, aluminum alloy 1100 (AA1100) coupons with nominal dimensions of 2.5 cm × 0.65 cm × 0.15 cm were irradiated in sealed Pyrex ampules (10 cm long × 10 mm diameter/ pristine sample ampule was 7.5 cm long). The gamma radiation source was ^{60}Co and the calculated absorbed doses for the samples ranged from 492 to 1104 kGy. There are inherent test time optimizations that result in a limited exposure dose during the initial testing. As a fiducial reference point, the maximum dose obtained here (1104 kGy) represents just a few months of exposure that moderately cooled fuel (<10 years since reactor discharge) may experience at the onset of extended dry storage. This corresponds to less than 1% of the cumulative cladding dose expected from the first 100 years of storage.

The cover gas in the ampules was either nitrogen or argon. An initial test set used air as a cover gas but found no free H_2 after irradiation. This was assumed to be due to back reactions with the oxygen (O_2) in the air. The humidity levels in the ampules were also varied from 0 to 100% RH, and this was assumed to cause a commensurate variety of surface adsorbed (physisorbed) water.

3.2 Hydrated Oxide Test Specimens

The test specimens with hydrated oxides were laboratory-grown by immersion in a water bath for 29 days at 95° C. The oxide thicknesses were estimated by weight gain calculations and cross-sectional scanning electron microscopy (SEM) data to be approximately 5.4 microns thick on average. As determined by X-ray diffraction (XRD) in reference 1, the hydrated oxide consisted of bayerite ($Al(OH)_3$, alternatively written as $Al_2O_3{\bullet}3H_2O$) with minor indications of boehmite (AlOOH, alternatively written as $Al_2O_3{\bullet}H_2O$). The water/hydrogen associated with this hydrated oxide is referred to as chemisorbed water, while the surface water film is referred to as physisorbed water. Tests reported in reference 2 were with non-oxidized aluminum samples to have comparison data for specimens with no chemisorbed water.

3.3 Hydrogen Generated

The quantity of H_2 that was generated by radiolysis of the water and hydroxyl groups associated with the sample and present in the ampule atmosphere following irradiation was measured. The quantity of H_2 versus absorbed gamma dose represents the primary data result from these tests. The source of H_2 is from the physisorbed and/or chemisorbed water and related hydroxyl groups present on the samples. Test runs using blank ampules with no Al samples but with varying RH resulted in no measurable H_2 release with radiation [1]. The H_2 generated in the ampules was measured by crushing the irradiated ampules in a Tygon tube and using an argon purge gas to quantify the amount of radiolytically generated H_2 by using an SRI Instruments gas chromatograph (GC) equipped with a Thermal Conductivity Detector (TCD).

3.4 Energy Deposition

An essential aspect of radiolysis testing of hydrated-oxide-on-aluminum substrates is the evaluation of energy deposition. Radiolytic yields (*G*-values) are typically evaluated by partitioning the amount of energy deposited into the material as a function of that material's constituent electron density [4]. It is postulated that energy deposited into the substrate, as in this case, can be transmitted to the attached oxide, and contribute to its radiolytic degradation [1, 5]. Thus, there are two energy deposition schemes that can be performed to compute radiolytic H_2 yield dependency on energy deposition:

- energy deposition into the hydrated oxide material only (i.e., the thin oxide film) on the aluminum substrate surface, or
- energy deposition into the oxide and substrate as a complete system.

The latter will result in a lower $G(H_2)$ value than that calculated with consideration of the energy deposited into just the oxide film.

For this present evaluation the calculated energy deposition into both the oxide and the aluminum substrate was used as the dose. This facilitates the comparison of H_2 generation from the different sample morphologies (i.e., oxidized surfaces versus non-oxidized surfaces). The reported G-value determinations [1, 2] are not included in this present evaluation.

4.0 Evaluations

4.1 Surface Adsorbed (Physisorbed) Water

Molecularly thin water films deposit on surfaces as a function of humidity. References 6, 7 and 8 present information regarding the range of molecular layers of water on metal oxide surface versus environmental humidity. A summary of the reviewed literature indicates that for humidity levels between 0% and 20%, a partial to a single monolayer film of adsorbed water typically exists on the surface. For humidity of 20% to 50%, the surface film increases to two monolayers. Above ~50% RH the number of molecular water layers significantly increases.

While the exact relationship between number of monolayers and humidity varies with surface condition it is assumed that for tests at near 0% RH there exists only a small degree of surface water. At levels near 40% there is full coverage with about one molecule thick water, and at 90% RH there are multiple monolayers of physisorbed water. Figure 2 from reference 6 is for hematite, Fe_2O_3, and shows the relationship between RH and water layers. The results from the hematite study are consistent with referenced reports for aluminum oxide surfaces [7, 8].

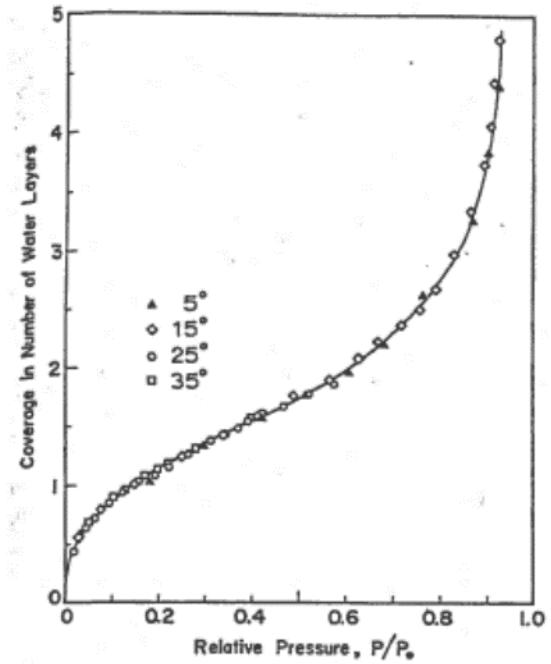

Figure 2. Water layer coverage on iron oxide as a function of relative water vapor pressure or RH. [6]

In addition to surface films, another related source of physisorbed water is surface pores, crevices, and capillary condensation. Per reference 6, "*The extent of capillary condensation is a function of the physical characteristics of the open porosity, such as pore size. These characteristics are not well known and can vary widely.*" Quantification of capillary condensation is beyond the scope of this present evaluation; however, it is recognized as a potential source for additional amounts of physisorbed water and may account for some H_2 release from surfaces tested in a 0% RH environment.

4.2 Chemisorbed water

Energy Dispersive Spectroscopy (EDS) analysis has shown that the surface hydrated oxide on the aluminum samples consists primarily of bayerite ($Al_2O_3 \cdot 3H_2O$) with some boehmite ($Al_2O_3 \cdot H_2O$). Based on their molecular weights, about 36% (MW of $3H_2O$ / MW of $Al_2O_3 \cdot 3H_2O$ = 54/156 = 0.36) of the bayerite (or gibbsite) weight is water and 15% (MW of H_2O / MW of $Al_2O_3 \cdot H_2O$ = 18/120) of the boehmite weight is water. This is assumed to be the amount of chemisorbed water available to potentially generate radiolytic H_2. To be discussed in detail in a separate report, the quantity of chemisorbed water (and H_2) present in a nominal oxide of 5 microns thick far exceeds the quantity of physisorbed water/H_2 on the oxide surface. This is also the conclusion reached by Wertsching in reference 9.

4.3 Hydrogen Generation Data from Gamma Irradiation

Two sets of H_2 generation data were measured and reported in references 1 and 2. The data from oxidized specimens (reference 1) is summarized in Table 1.

Table 1. Summary of molecular hydrogen measurements for gamma irradiation of aluminum specimens with a surface oxide. [1]

Fill Gas	**Relative Humidity** (%)	**Absorbed Gamma Dose** (kGy)	**H_2 Generated** (µL)	**Oxide Thickness** (µm)
Argon	1	537	7.5	5.01
Argon	49	543	8.8	5.36
Argon	91	556	8.7	5.49
Argon	0	1070	10.2	5.18
Argon	49	1081	14.2	5.5
Argon	93	1110	14	5.44
Nitrogen	0	495	1.1	5.15
Nitrogen	51	492	2.1	5.35
Nitrogen	100	498	2.3	5.24
Nitrogen	1	894	3.1	5.17
Nitrogen	52	978	7	5.52
Nitrogen	92	991	6.2	5.58

The data from Table 1 is plotted in Figure 3, from which it is observed that:

- The full data range (all doses considered) trends of H_2 generation with absorbed gamma dose is not linear, given the intercept should be zero H_2 generation at zero absorbed dose, and that an equilibrium has not yet been reached.
- The initial H_2 quantities in the argon atmosphere are higher than the quantities measured in the nitrogen atmosphere.
- The H_2 values for the 0-1% RH are lower than higher humidity samples within each atmosphere group.

It is postulated that some chemical reactions are active at the initial absorbed dose values that result in an initially lower level of measured H_2 in the nitrogen atmosphere. The relative difference in initial H_2 values is also observed in the non-oxidized sample irradiations in a subsequent section of this report. The relatively lower H_2 quantities associated with the 0-1% RH conditions are postulated to be due to the limited availability of physisorbed water for radiolysis compared to the high RH environments. This trend at the initial dose levels indicates that the H_2 generation rate in an argon atmosphere is greater than in a N_2 atmosphere. However, the rates (curve slopes in Figure 3) at the higher doses are essentially equivalent for both atmospheres. This observation is discussed in more detail in section 4.4.

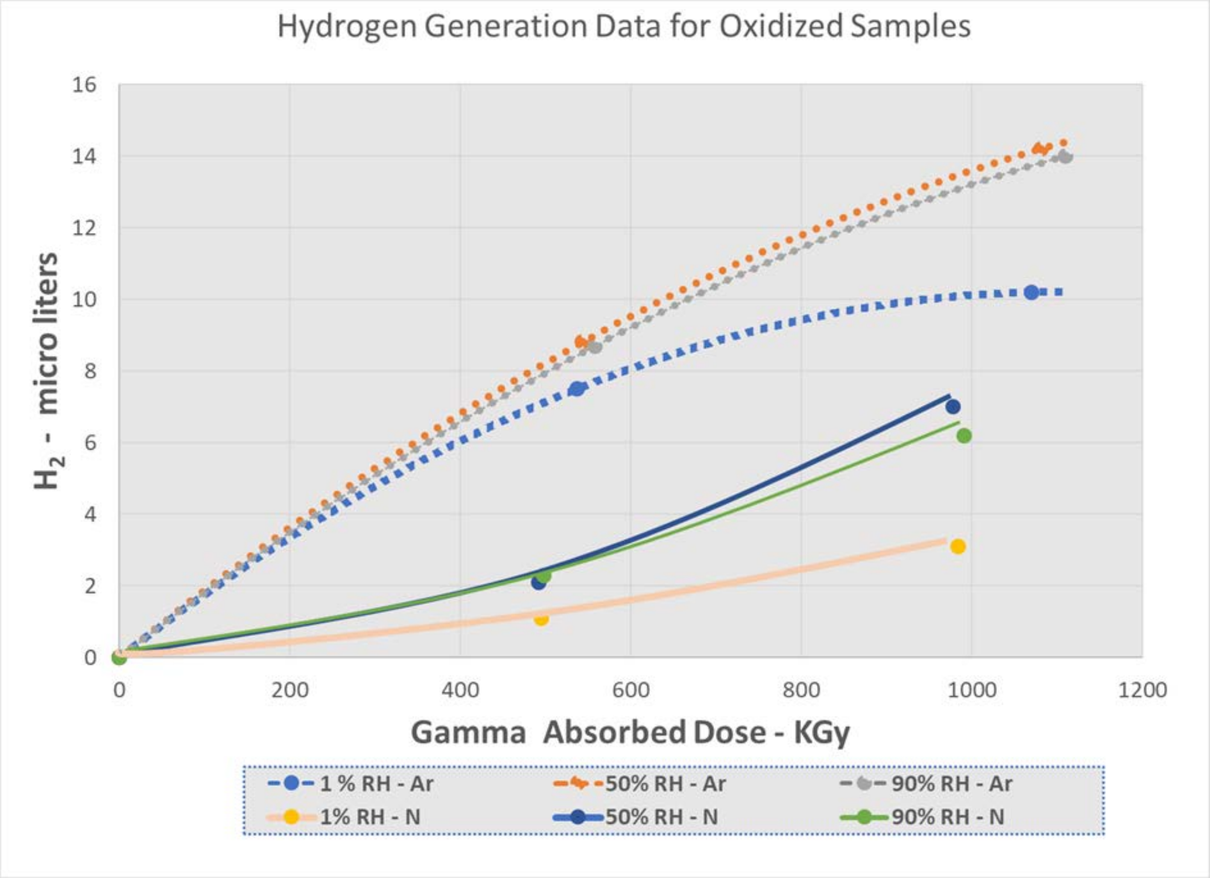

Figure 3. Molecular hydrogen generation measurements from gamma irradiation of oxidized specimens in argon and nitrogen atmospheres [1].

In reference 2, a set of data was reported for the gamma radiation of non-oxidized (pristine) aluminum samples. The tests included different humidity levels. For these samples, it is assumed there is no significant surface oxide source for chemisorbed water even though there is probably a very thin oxide film present due to preparation procedure and the reactive nature of aluminum surfaces to oxygen. [10] The results are shown in Figure 4 for nitrogen atmospheres and Figure 5 for argon atmospheres.

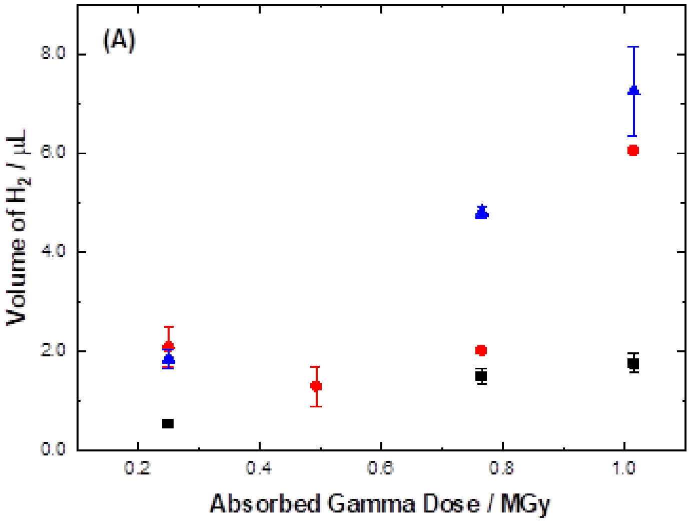

Figure 4. Volume of H_2 produced from the gamma irradiation (46 Gy min^{-1}) of non-oxidized aluminum-1100 coupons in a nitrogen atmosphere at ambient temperature: 0% (■), 40% (●), and 80% (▲) relative humidity [2].

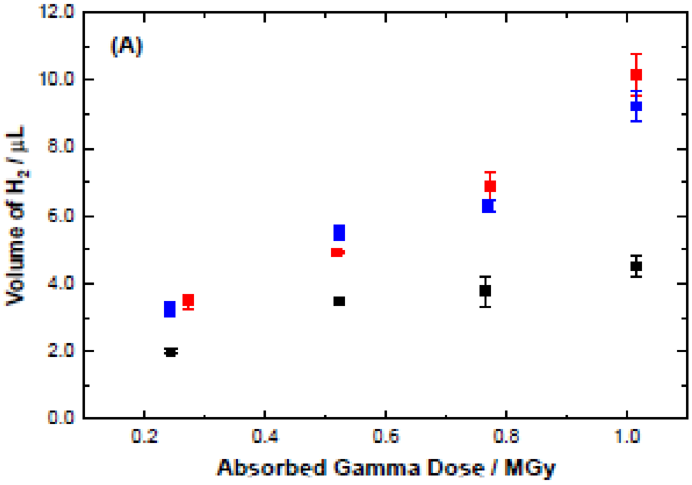

Figure 5. Volume of H_2 produced from the gamma irradiation (46 Gy min^{-1}) of non-oxidized aluminum-1100 coupons in an argon atmosphere at ambient temperature: 0% (■), 40% (●), and 80% (▲) relative humidity [2].

The observations from the non-oxidized specimen data trends indicate:

- The trends of initial H_2 generation versus absorbed gamma dose are non-linear for low doses (given the expected zero intercept), which is consistent with the aforementioned oxidized samples; however, the higher dose data appears to exhibit linearity, ($\Delta H_2/\Delta$dose is linear), particularly for the argon samples.
- A higher initial H_2 value is observed for argon atmospheres compared to nitrogen, once again, consistent with oxidized specimen observations.
- The 0% RH samples produce less H_2 compared with the 40% and 80% RH samples, much like the oxidized samples. Further, the 0% RH trend lines tend to show plateauing at the higher doses which may be due to the (limited) availability of physisorbed water.
- Most of the data show consistent trends except the two 40-50% RH data points in nitrogen at the intermediate doses, where they appear to divert from the general trend of approximation to the higher humidity samples in both the oxidized (50% RH) and non-oxidized (40% RH) argon data sets. It is not clear if these are outlier data points or represent a repeatable effect.

Values for dose and H_2 from the charts are listed in Table 2. The potentially outlier data points for 40% RH nitrogen are shaded.

Table 2. Summary of hydrogen generation from non-oxidized specimens

Fill Gas	**Relative Humidity** %	**Absorbed Gamma Dose** (kGy)	**H_2 Generated** (μL)
Nitrogen	0	250	0.54 ± 0.09
Nitrogen	0	770	1.50 ± 0.17
Nitrogen	0	1015	1.76 ± 0.20
Nitrogen	41	250	2.09 ± 0.40
Nitrogen	44	490	1.29 ± 0.39
Nitrogen	45	770	2.02 ± 0.06
Nitrogen	41	1015	6.05 ± 0.07
Nitrogen	79	250	1.84 ± 0.19
Nitrogen	78	770	4.80 ± 0.10
Nitrogen	81	1015	7.24 ± 0.90
Argon	0	242	2.00 ± 0.05
Argon	0	520	3.50 ± 0.09
Argon	0	770	3.78 ± 0.45
Argon	0	1015	4.50 ± 0.28
Argon	25	270	3.48 ± 0.21
Argon	44	520	4.92 ± 0.02
Argon	41	770	6.86 ± 0.41
Argon	41	1015	10.17 ± 0.61
Argon	82	240	3.23 ± 0.19
Argon	87	520	5.50 ± 0.21
Argon	84	770	6.28 ± 0.15

4.4 Hydrogen Generation Rate for Input to Performance Model

Hydrogen generation rate is a primary input to the coupled thermal-chemical system model of the performance of aluminum-clad spent nuclear fuel in a dry storage canister (ASNF-in-canister) over its storage life. The hydrated oxides on ASNF, and not the physisorbed water, is the major water source of potential radiolytic hydrogen for the ASNF-in-canister system. The hydrogen generation rate from chemisorbed-only water is the intended input to the model.

There is a degree of non-linearity at the initial absorbed doses associated with some transitional mechanisms, including back-reactions. While these data sets have a limited range in gamma exposure, if it is postulated that the data points near 500 and 1000 kGy are representative of a regime that is dominated by physisorbed water, then a comparison of the rates based on those data points is useful in comparing the effects of humidity and atmosphere. This absorbed gamma dose is equivalent to about three-months of radiation exposure (total dose) during dry storage and thus, is significantly lower than the envisioned exposure during extended (up to and >50 years) storage.

Figure 6 combines the data from irradiation of both non-oxidized and oxidized samples in an argon atmosphere. Only values with doses above 500 kGy are included to minimize the transitional effects of the low dose results. The slopes of each curve are included and represent the relative rates of H_2 generation for the higher doses. The samples in the higher RH environments, 40% to 92% RH, have similar slopes/rates ranging from 0.0075 to 0.0107 μL kGy^{-1}. The samples, both pristine and with oxide, that were tested in the 0 to 1% RH range had lower rates of 0.002 to 0.005 μL kGy^{-1}. The similar slopes at the higher humidity indicate that there is no significant difference in H_2 production rates related to the presence or absence of a surface oxide. The oxidized sample at nominally 1% RH and with a larger surface area due to the oxide morphology could have some physisorbed water along with the chemisorbed, which could explain the difference in H_2 generation rates between the non-oxidized and oxidized sample at the low RH. This is predicated on the assumption that the "pristine" sample has only a very thin, 2 to 5 nanometers, Al_2O_3 oxide. If there is no significant chemisorbed water on the pristine samples, the only source for the H_2 generation is via the radiolysis of physisorbed water, which is consistent with the observed lower H_2 production rate for the low humidity environment.

Extended testing at higher doses would provide data to verify physisorbed water as the initial H_2 source for pristine samples, since the amount of physisorbed water is expected to be significantly lower than the chemisorbed water content, so it would be exhausted first in a high-dose experiment. Alternatively, conditioning of the test specimens (hydrated-oxides-on-aluminum substrates) with a thermal "drying" treatment to remove, as practicable, physisorbed water would provide a specimen design in which H_2 generation would be from predominantly chemisorbed water.

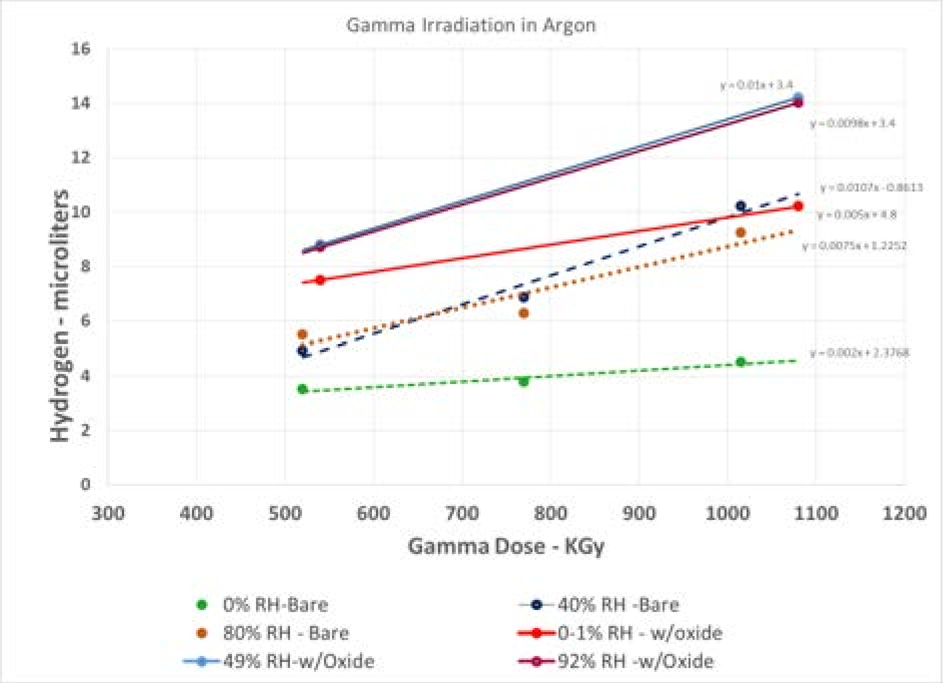

Figure 6. Combined data plot for pristine and oxidized samples in argon.

Figure 7 is a similar plot for the samples tested in nitrogen environments and provides similar results. The rates for both non-oxidized and oxidized samples in the 40% to 92% RH environments, where multilayers of water are expected, are also similar. The high RH data ranges from 0.008 to 0.0101 µL kGy^{-1}, and the low RH tests have both lower relative H_2 levels and lower rates. The data is limited, but the observation is that all of the high RH data, both in argon and nitrogen and with oxide and without, are consistently close in H_2 generation rates. This observation supports the postulation that the bulk of this initial H_2 is coming from radiolysis of the physisorbed water. Additional testing is needed to better understand the mechanisms occurring specific to this system.

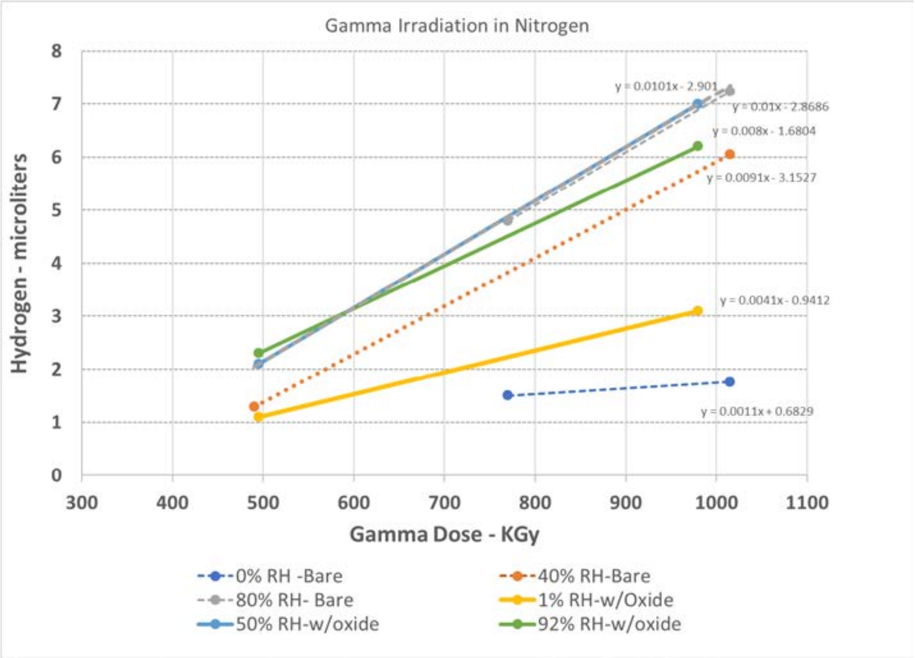

Figure 7. Combined data plot for non-oxidized and oxidized samples in nitrogen.

Table 3 summarizes the measured H_2 generation rates for the various conditions observed in Figure 6 and Figure 7. The data in this table is calculated with the data from 500 kGy and higher dose and thus reduces the impacts of non-linear rates at the low-initial dose levels. If the data point of 0 hydrogen at 0 dose is included in a linear plot, then the rates for the oxidized samples reported in reference 1 range from 0.0052 to 0.0125 µL/ kGy which is a similar range to the range in Table 3 (0.002 to 0.0107 µL/ kGy).

As previously noted, the rates for all of the >40% RH tests have a similarly high rate, and the low RH tests show significantly lower H_2 generation rates for both oxidized and non-oxidized samples. This provides support for the postulation that, for the initial dose H_2 generation regime, physisorbed water is the primary source for the high hydrogen generation rates observed in the high humidity conditions, since the presence or absence of oxide and chemisorbed water is the same for both high and low humidity.

Table 3. Molecular hydrogen generation rates in µL kGy^{-1}.

Atmosphere	Nominal Humidity	H_2 Generation Rate (µL kGy^{-1})	
		Pristine	**Oxidized**
N_2	0 - 5 %	0.0011	0.0041
N_2	40 -51 %	0.0091	0.0101
N_2	80 - 92%	0.010	0.008
Ar	0 -5 %	0.002	0.005
Ar	40 - 49 %	0.0107	0.010
Ar	80 - 92 %	0.0075	0.0098

5.0 Conclusions

The following statements are preliminary findings and postulated conclusions.

5.1 During the low gamma dose regime, represented by absorbed doses less than 300 kGy (for this set of tests), the H_2 generation rate is not linear with absorbed gamma dose. Some transitional mechanisms are occurring that are gaseous environment dependent. However, this evaluation suggests that the H_2 generation rates are similar for nitrogen and argon at higher dose levels.

5.2 Tests in humidity at and above 40% RH

5.2.1 There are assumed to be multilayers of physisorbed water on the samples for the humidity levels of 40% and above. The H_2 generation rates are equivalent at higher dose levels for both non-oxidized and oxidized samples in both N_2 and Ar atmospheres, ranging from 0.0075 to 0.0107 µL kGy^{-1}. This supports a conclusion that the H_2 generation rate will be independent of the cover gas, nitrogen or argon, at exposures relevant to several months of fuel storage.

5.2.2 It is assumed that there was essentially no chemisorbed water on the non-oxidized specimens. Due to the similar generation rates for oxidized and non-oxidized specimens, it is concluded that the H_2 being generated from the specimens in moderate-to-high humidity is primarily coming from the physisorbed surface water.

5.2.3 There is a difference in the hydrogen generation rate in the N_2 and the Ar environments at initial low doses versus the higher doses (>500 kGy). The data also suggests that there is a mechanism(s) present during the initial/low gamma dose regime in the N_2 environment more so than in the Ar that results in a reaction mechanism that diminishes H_2 production relative to the Ar environment.

5.3 Tests at or near 0% RH

5.3.1 The H_2 generation rates for the samples in low humidity, 0 to 5%, are significantly lower than the rates for samples in the higher humidity levels. This is postulated to be related to the very limited availability of physisorbed water for the low humidity samples.

5.3.2 The generation rates for the low-RH oxidized samples at higher dose rates are equivalent between the different atmospheres, supporting the prior conclusion that there is no significant difference in steady generation rates between the N_2 and Ar atmospheres.

5.3.3 The limited data does suggest that there is a difference in the initial radiolytic generation rates between the non-oxidized (pristine) specimens and the oxidized specimens. It is postulated that for the low humidity exposure there is less physisorbed water available for the pristine sample in comparison to the oxidized sample. This is a likely due to the low humidity causing low physisorbed water with the relatively low surface area and lack of surface crevices and pores in the pristine specimens that are characteristic of the oxide surface.

5.4 The data is limited and precludes a clear conclusion on the rate contribution (if any) from chemisorbed water, but it does support, when compared to the high humidity values, the significant (initial) contributions from physisorbed water. The data and this evaluation apply for the initial gamma doses and do not reflect the steady-state conditions expected with higher/longer doses and related back-reactions.

5.5 Estimates of the relative physisorbed water to the chemisorbed water show (to be reported separately) that the chemisorbed water reservoir is significantly larger than the physisorbed water reservoir for nominal fuel initial (pre-dried) conditions. Based on the observed lower hydrogen generation rate on oxidized samples in low humidity, and with the hydrogen generation attributed to the physisorbed water, the rates observed for the current high humidity samples are probably not sustained once the physisorbed inventory is depleted.

5.6 Additional radiolysis testing in calendar year 2020 (CY20) is being planned to allow better discrimination of physisorbed vs. chemisorbed contributions to H_2 yield and the dose regimes over which they dominate. Data for thermally-conditioned (“dried”) hydrated oxides will also be developed. The completion of the CY20 testing will lead to identification of the “steady-state” H_2 generation rates that would be input to the ASNF-in-canister performance model to provide the best estimate of the evolution of gas composition over decades of dry storage.

6.0 References

[1] Parker-Quaife, E.H.; Horne, G.P.; Heathman, C.R.; Verst, C; and Zalupski, P.R.; “Radiation- Induced Molecular Hydrogen Gas Generation by Pre-Corroded Aluminum Alloy 1100,” INL/EXT-19-55202 Rev 1; July 2019.

[2] Parker-Quaife, E.H.; Horne, G.P.; Heathman, C.R.; and Zalupski, P.R.; “Radiation-Induced Molecular Hydrogen Gas Generation by Pre-Corroded Aluminum Alloy 1100,” FY20 December Update; Center for Radiation Chemistry Research, Idaho National Laboratory, Idaho Falls, ID 83415, USA.

[3] Connolly, M., et. al., INL/EXT-17-43908, “Aluminum Clad Spent Nuclear Fuel Long Term Dry Storage Technical Issues Action Plan – Technical and Engineering Activities,” INL, November 2017.

[4] Swallow, A.J., “Radiation Chemistry: An Introduction,” Wiley, 1973.

[5] Petrik, N.G.; Alexandrov, A. B.; and Vall, A. I.: “Interfacial Energy Transfer during Gamma Radiolysis of Water on the Surface of ZrO_2 and Some Other Oxides,” Journal of Physical Chemistry, B 2001105, 5935-5944.

[6] Ebner, E.; Jordan, R.; Bates, S.; "Literature review of the Drying Characteristics of Uranium, Aluminum, Iron, and Spent Fuel Corrosion Products," INEEL/EXT-2000-01038, Feb 2001.

[7] Yan, Ben-Da et al; “Water Adsorption and Surface Conductivity Measurements on Alpha-Alumina Substrates,” IEEE Transactions on Components, Vol 10 Issue 2.

[8] Al-Abadleh, H.A and Grassian, V. H., “FT-IR Study of Water Adsorption on Aluminum Oxide,” Langmuir 2003, Vol 19 pages 341 – 347.

[9] Wertsching. A.K., "Materials Interactions on Canister Integrity During Storage and Transport," DOE/SNF/REP-104, December 2007.

[10] Vargel, C. (Eds.), “Introduction to The Corrosion of Aluminium, Chapter B.1 Corrosion of Aluminium,” Elsevier, 2004, pp. 81-109.

[11] Kaddissy, J., “Hydrogen Production from Irradiated Aluminum Hydroxide and Oxyhydroxide,” Material Chemistry, Université Paris-Saclay, 2016. English. NNT: 2016SACLS253. tel-01531842.

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