Milestone 1.2.9: Radiolytic Gas Generation Measurements from Helium-Backfilled Samples of AA1100 and AA6061 Coupons

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ABSTRACT

Nearly 18 metric tons of aluminum-clad spent nuclear fuel is safely managed by the U.S. Department of Energy. These assemblies are currently in interim storage, with the intention of extended storage (>50 years) until final disposal. Strategies for the continued safe storage of this material are under evaluation, of which a key criterion is the extent of molecular hydrogen gas (H₂) formation from the radiolysis of hydrated (oxy)hydroxide aluminum corrosion layers arising from in-reactor and wet storage conditions. Radiation-induced H₂ formation has the potential to compromise cladding and storage canister integrity, in addition to promoting the formation of unfavorable gaseous environments. Consequently, understanding this radiation-induced phenomenon is essential for the development of predictive modeling capabilities to support technical considerations and the identification of radiation related challenges for the extended storage of aluminum-clad spent nuclear fuel. Here, we report radiolytic H₂ yields (G-values, G(H₂)) from the gamma irradiation of “pristine” and pre-corroded aluminum coupons in helium (He) environments as a function of alloy composition (AA1100 and AA6061), relative humidity, and absorbed gamma dose. Measured yields were lower than corresponding values reported for argon environments, a positive result for proposed extended dry storage strategies that would employ helium as a backfill gas. Interestingly, the presented G(H₂)ₚₑ values are comparable to those previously measured in nitrogen environments, suggesting a He-mediated H₂ inhibition process, attributed here to Penning ionization.
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## ACRONYMS

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<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
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<tbody>
<tr>
<td>AA1100</td>
<td>aluminum alloy 1100</td>
</tr>
<tr>
<td>AA6061</td>
<td>aluminum alloy 6061</td>
</tr>
<tr>
<td>ASNF</td>
<td>aluminum-clad spent nuclear fuel</td>
</tr>
<tr>
<td>DOE</td>
<td>Department of Energy</td>
</tr>
<tr>
<td>GC</td>
<td>gas chromatography</td>
</tr>
<tr>
<td>RH</td>
<td>relative humidity</td>
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</tbody>
</table>
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1. INTRODUCTION

The U.S. Department of Energy (DOE) is currently evaluating options for the safe extended storage of almost 18 metric tons of aluminum-clad spent nuclear fuel (ASNF) [1]. One of the technical challenges associated with this task is understanding the extent of molecular hydrogen gas (H$_2$) generation from the radiation-induced decomposition of hydrated (oxy)hydroxide aluminum corrosion layers. These ASNF corrosion layers are a consequence of in-reactor and subsequent wet storage conditions—a combination of radiation, elevated temperature, and water contact—that promote aluminum corrosion [2,3]. The resulting aluminum (oxy)hydroxides (e.g., boehmite, gibbsite, and bayerite) and their adsorbed inventory of water are susceptible to radiolysis by gamma fields originating from the radioisotopic contents of the ASNF, which ultimately leads to the formation of H$_2$ [4-12]. The generation of H$_2$ in ASNF storage casks/canisters is not ideal as it may lead to aluminum alloy embrittlement, cask/canister pressurization, and the formation of explosive and/or flammable gas mixtures [13-16]. Consequently, the radiolytic formation of H$_2$ from hydrated (oxy)hydroxide powders and corroded aluminum coupons has been extensively investigated to underpin H$_2$ formation mechanisms and their dependence on the absorbed radiation dose, extent of corrosion, gaseous environment, relative humidity (RH), and temperature [4-12]. The data gleaned from these studies are essential for the development of predictive computer models to support technical considerations and the identification of radiation-related challenges for the extended storage of ASNF.

Research performed as part of the DOE Office of Environmental Management-Technology Development (EMTD) Technical Basis for Extended Dry Storage of Aluminum-Clad Spent Nuclear Fuel initiative demonstrated that the radiolytic yield of H$_2$ from corroded aluminum coupons was strongly dependent on the gaseous environment (air, nitrogen, or argon) in which the coupons were irradiated [12]. A precedence for increasing radiolytic yield ($G$-value) with increasing chemical inertness (air < nitrogen < argon) was observed. These findings suggested that irradiation of ASNF in helium (He) – which has been proposed as the backfill gas for the extended (>50 years) dry storage of ASNF in the standard DOE canister [17-19] – may promote the formation of larger yields of H$_2$ than previously measured for argon (Ar). This hypothesis was preliminarily tested for aluminum alloy 1100 (AA1100) coupons, which did find different yields of H$_2$ in He compared with Ar [20]. However, the reported H$_2$ data was acquired using a mercuric reduction gas detector, which was found to saturate at low H$_2$ concentrations and struggle with reproducibility. Consequently, this hypothesis requires reevaluation in addition to an extension to other aluminum alloy types. The latter parameter is important because the aforementioned radiation studies on aluminum metal coupons focused on AA1100, whereas the DOE ASNF inventory consists of a variety of aluminum alloy types, including AA1100 and AA6061 [1]. As different alloys have different elemental compositions, this may influence the structure and minerology of the aluminum corrosion layers, and ultimately affect the radiation response of the system.

In response to these uncertainties and the question of alloy effects, we report H$_2$ data from the gamma irradiation of pristine and pre-corroded AA1100 and AA6061 coupons in He environments at ambient temperature over a range of RH. The presented yields were measured using a benchmarked thermal conductivity detector.
2. EXPERIMENTAL METHODS

2.1 Materials

AA1100 and AA6061 coupons (2.5 cm × 0.65 cm × 0.15 cm) were purchased from Metals Samples Company - Alabama Specialty Products, Inc. Aluminum alloys were selected based on their abundance in the United States ASNF inventory [1]. Acetone (HPLC Plus, ≥ 99.9%) and ethanol (absolute, ≥ 99.8%) were supplied by MilliporeSigma. Helium was purchased in its highest available purity from Norco. Ultra-pure water (18.2 MΩ·cm) was used for all water applications. All AA1100 and AA6061 coupons were prepared and flame-sealed as previously described [12].

2.2 Gamma Irradiations

Irradiations were performed using the Idaho National Laboratory Center for Radiation Chemistry Research Foss Therapy Services Cobalt-60 Irradiator unit. Samples comprised individually flame-sealed borosilicate glass ampules containing a single pristine (cleaned only) or corroded (cleaned and corroded) AA1100 or AA6061 coupon in a He gaseous environment at either 0%, 50%, or 100% RH. Samples were loaded into a multi-position sample holder and irradiated at ambient irradiator temperature (~45°C, as determined using a calibrated NI USB-TC01 Single Channel Temperature Input Device equipped with a K-type thermocouple) over several days to achieve the desired radiation dose. Dose rates (Gy min⁻¹) were determined by chemical dosimetry using Fricke solution [21] and were subsequently corrected for the decay of cobalt-60 (τ₁/₂ = 5.27 years; Eγ₁ = 1.17 MeV and Eγ₂ = 1.33 MeV) and aluminum metal electron density (0.8673) [22]. G-values (μmol J⁻¹) were calculated from linear slopes fitted to measured H₂ concentrations in μmol kg⁻¹ of material irradiated versus absorbed gamma dose.

2.3 Gas Chromatography

Gas chromatography (GC) was used for the quantification of H₂. The GC methodology used here employed a Shimadzu Co. (Kyoto, Japan) Nexus GC-2030 gas chromatograph equipped with a benchmarked thermal conductivity detector set at 200°C. The injection port temperature was 150°C with a split ratio of 15. The carrier gas was He with a linear velocity of 50.0 cm s⁻¹. The column (Restek, #19722 Molecular Sieve 5 Å) had an oven temperature profile of 40°C for 2 minutes, followed by a ramp to 50°C over 20 seconds, and finally a 1-minute hold, for a total run time of 3.33 minutes per injection. All injections were repeated in triplicate, and the results were averaged. This method has an estimated error of ≤10% and limits of detection of 0.01–1% H₂ at the 95% confidence level. Quality control checks were performed daily to confirm known concentrations of H₂ relative to measured calibration curves.

Sampling used a crush-tube method, wherein the flame-sealed ampules containing the Al coupons were cracked inside a length of tubing (Nalgene, 8005 braided PVC) that was fitted with a septum on one end. The headspace of the tubing was then sampled in 100 μL aliquots with a gas-tight syringe (Hamilton, Model 1810 RN) and injected into the GC. The ampule and tubing headspace volumes were determined by filling with water and weighing before and after cracking the ampules. The pressure in the tubing headspace was calculated iteratively using the ideal gas law (PV = nRT) with the calculated gas yields, the measured headspace volumes for the tubing and the ampule, and the known pressure of He at which the ampule was sealed. The resulting yields of H₂ are reported in μmol kg⁻¹ of the aluminum coupon, base metal and corrosion layer.
3. RESULTS AND DISCUSSION

The radiolytic formation of H$_2$ from the gamma irradiation of AA1100 coupons in He environments is shown in Figure 1 for 0% (A), 50% (B), and 100% (C) RH. The corresponding $G$-values are presented in the figures in addition to Table 1.

![Figure 1](image)

**Figure 1.** Concentration of H$_2$ (μmol kg$^{-1}$) as a function of absorbed gamma dose from the irradiation of pristine (■) and corroded (○) AA1100 coupons in He environments at 0% (A), 50% (B), and 100% (C) RH at ambient irradiator temperature. Solid lines are linear fits to data for $G$-value calculation.

For all three RH conditions the concentration of H$_2$ increases linearly with absorbed gamma dose, in agreement with previous work [12]. This is predominantly a consequence of adsorbed water radiolysis [23]:

\[ \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{O}^*, \text{e}_{\text{aq}}^-, \text{H}^+, '\text{OH}, \text{H}_2, \text{H}_2\text{O}_2, \text{H}_{\text{aq}}^+ \]

(1)

\[ \text{H}_2\text{O}^* \rightarrow \text{H}_2 + \text{O} \]

(2)

\[ \text{e}_{\text{aq}}^- + \text{e}_{\text{aq}}^- + 2\text{H}_2\text{O} \rightarrow \text{H}_2 + 2\text{OH}^- \]

(3)

\[ \text{e}_{\text{aq}}^- + \text{H}_{\text{aq}}^+ \rightarrow \text{H}^+ \]

(4)

\[ \text{e}_{\text{aq}}^- + \text{H}^+ + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{OH}^- \]

(5)

\[ \text{H}^+ + \text{H}_2\text{O} \rightarrow \text{H}_2 + '\text{OH} \]

(6)

\[ \text{H}^+ + \text{H}^+ \rightarrow \text{H}_2 \]

(7)
and given that the rate of H₂ production did not deviate from linearity, indicates that the coupons must have a sufficient excess of adsorbed water. This indicates that sufficiently higher absorbed doses are necessary to attain a steady-state H₂ yield. As with our previous work [12], corroded coupons afforded higher yields of H₂ compared with those from pristine coupons. This is a consequence of the attendant (oxy)hydroxide corrosion layers providing a greater surface area for water adsorption, while also providing an additional source of radiolytic H₂ [24-26]. It is also evident from the corroded AA1100 coupon data in Figure 1 and the corresponding G-values in Table 1 that the yield of H₂ increased with RH. This observation is in partial agreement with previous work [12], however, here we see a continued increase in G(H₂)ₜₚ above 50% RH, whereas previously we observed a decrease. This discrepancy is likely a result of there being significantly fewer data points collected by our previous study. Here we executed a more extensive study.

Table 1. Comparison of H₂ G-values for gamma-irradiated pristine and corroded AA1100 and AA6061 coupons in He environments at 0%, 50%, and 100% RH.

<table>
<thead>
<tr>
<th>Coupon State</th>
<th>Alloy</th>
<th>RH (%)</th>
<th>G(H₂) (10⁻⁴ µmol J⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine</td>
<td>AA1100</td>
<td>50</td>
<td>1.04 ± 0.08</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100</td>
<td>0.90 ± 0.10</td>
</tr>
<tr>
<td></td>
<td>AA6061</td>
<td>0</td>
<td>0.38 ± 0.05</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50</td>
<td>0.52 ± 0.06</td>
</tr>
<tr>
<td>Corroded</td>
<td>AA1100</td>
<td>0</td>
<td>1.15 ± 0.05</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50</td>
<td>2.92 ± 0.04</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100</td>
<td>4.19 ± 0.10</td>
</tr>
<tr>
<td></td>
<td>AA6061</td>
<td>0</td>
<td>2.78 ± 0.10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50</td>
<td>2.18 ± 0.09</td>
</tr>
</tbody>
</table>

A comparison of AA1100 G(H₂)ₜₚ values with previously reported yields for irradiations in Ar clearly show a decrease in the yield of H₂ in the presence of He under similar adsorbed gamma doses [12]. Further, the H₂ yields measured here are closer to those reported for nitrogen (N₂) [12]. For example, the gamma irradiation of corroded AA1100 in 50% RH afforded G(H₂) = 2.92 ± 0.04 in He, 4.5 ± 0.1 in N₂, and 9.6 ± 0.6 in Ar [12]. These observations are indicative of a He-mediated H₂ inhibition process, attributed here to Penning ionization:

\[
\text{He} \leftrightarrow \text{He}^*, \quad (8)
\]

\[
\text{He}^* + \text{H}_2 \rightarrow \text{He} + \text{H}_2^+ + e^-, \quad (9)
\]

whereby radiolytically generated excited states of helium (He*) possess energies in excess of the ionization potential of H₂ (15.4 eV vs. 24.59 eV for He [27]), thereby inducing H₂ ionization upon collision via the de-excitation of the He*. This phenomenon has been well characterized for the ionization of noble gases, some metals, and other small molecules, including H₂ [28-35]. This process is not accessible for Ar in this scenario owing to the similarity in the first ionization energies of Ar (15.76 eV) and H₂ (15.4 eV) [27]. The resulting ionized H₂ (H₂⁺) likely decomposes on the aluminum coupon surface (M):

\[
\text{H}_2^+ (\rightarrow \text{M}) \rightarrow \text{M-H} + \text{M-H}^+. \quad (10)
\]

This He inhibition observation is fortuitous for the current strategy for the extended dry storage of ASNF in He-backfilled canisters.

The radiolytic formation of H₂ from the gamma irradiation of AA6061 coupons in He environments is shown in Figure 2 for 0% (A) and 50% (B) RH. The corresponding G-values are presented in the figures in addition to Table 1. Similar to the trends seen for AA1100, the gamma irradiation of AA6061 coupons...
afforded a linear response in H₂ formation as a function of the absorbed gamma dose for both pristine and corroded conditions. However, for 0% RH (Figure 2 (A)), corroded AA6061 coupons exhibited a significantly higher rate of H₂ production compared to AA1100 coupons, affording G(H₂)He values of 2.78 ± 0.10 and 1.15 ± 0.05, respectively, as shown in Table 1. In contrast, when the RH was increased to ~50% (Figure 2 (B)), the inverse trend was observed (i.e., AA6061 coupons afforded a significantly lower yield of H₂ compared to AA1100, G(H₂)He = 2.18 ± 0.09 vs. 2.92 ± 0.04, respectively). These differences in response to RH during irradiation suggest differences between the chemical composition and minerology of the corrosion layers of the two alloys.

The two most common aluminum (oxy)hydroxides formed by the corrosion of aluminum-clad fuel in water-cooled reactors [2,3] are boehmite and gibbsite. Westbrook et al. demonstrated that boehmite is more susceptible to radiolytic H₂ production than gibbsite [10], further, the radiolytic yield of H₂ from gamma irradiated boehmite powders was shown to exhibit a negative correlation with RH, for which they reported a 76% drop in H₂ yield in going from ~0% RH to water vapor (~100% RH) [10]. Based on these observations and our findings, we postulate that the differences in H₂ production between AA6061 and AA1100 are due to a larger contribution of boehmite in the AA6061 corrosion layer. With regards to AA1100, we previously demonstrated that our corrosion conditions promote the formation of a multilayer, comprised of an amorphous layer at the interface with the aluminum metal, followed by a layer of boehmite, and then an outer crystalline layer of bayerite, an aluminum hydroxide polymorph/polypeptide [12]. The radiolytic yield of H₂ from this AA1100 corrosion multilayer was found to increase with RH, as shown in Table 1. A follow-up study is underway to investigate the differences in corrosion layer compositions between AA6061 and AA1100.

4. CONCLUSIONS

The purpose of this investigation was to re-evaluate the effect of He on the radiolytic yield of H₂ from irradiated pristine and corroded AA1100 coupons and extend this study to include other relevant aluminum alloy types. Gamma irradiation of AA1100 and AA6061 alloy coupons in dry (0% RH) and “wet” (≥50% RH) He environments afforded G(H₂)He values similar to those obtained for previously reported N₂ environments but significantly lower than those measured for Ar environments. The difference in radiolytic response between the two noble gas environments (He vs. Ar) was attributed to the ability of He to promote Penning ionization and ultimately the decomposition of H₂ under the investigated conditions.

Alloy composition (AA1100 vs. AA6061) was also found to have a significant effect on the rate and yield of radiolytic H₂ production, of which AA6061 exhibited a negative correlation with RH, in contrast
with AA1100. The difference in radiolytic response between the two alloys was ascribed to postulated differences in the composition of their respective corrosion layers.

Overall, the presented $G(H_2)_{He}$ values are important for the development of predictive computer models for evaluating the feasibility of extended storage of ASNF in He-backfilled canisters

5. ACKNOWLEDGMENTS

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6. REFERENCES

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