



Milestone 2.8: Preliminary Radiolytic Gas Generation Measurements from Helium-Backfilled Samples

December 2020

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ABSTRACT

The Department of Energy (DOE) is currently managing nearly 13 metric tons of aluminum-clad spent nuclear fuel (ASNF), and some of this ASNF will be placed in helium-backfilled canisters for extended (> 50 years) dry storage. Due to in-reactor and cooling pond conditions, oxyhydroxide corrosion layers have formed on the surface of the ASNF elements. These corrosion layers are susceptible to radiolysis and the formation of molecular hydrogen gas (H_2) due to the fuel's inherent radiation field. Consequently, a rigorous evaluation of the effect of helium gas on radiolytic H_2 production is necessary to support the "Technical Considerations and Challenges for Extended (> 50 years) Dry Storage of ASNF" program, especially as previous "Task 2 - Oxyhydroxide Layer Radiolytic Gas Generation Resolution" work demonstrated a significant effect of gas composition on the radiolytic yield (G -value) of H_2 . Here, we report preliminary G -values for the radiolytic formation of H_2 from the gamma irradiation of pre-corroded aluminum alloy 1100 coupons flame sealed in helium environments. Irradiations yielded $G(H_2)$ values of $(5.1 \pm 0.5) \cdot 10^{-4}$ and $(9.4 \pm 0.9) \cdot 10^{-4} \mu\text{mol J}^{-1}$ for pristine coupons, and $(10.1 \pm 0.4) \cdot 10^{-4}$ and $(15.1 \pm 1.2) \cdot 10^{-4} \mu\text{mol J}^{-1}$ for pre-corroded coupons for 0% and 50% relative humidity, respectively. These helium environment $G(H_2)$ values are between 28% and 58% higher than previously reported values for argon environments. This enhancement is attributed to the significant difference in first ionization energy between helium (24.59 eV) and argon (15.76) facilitating additional processes (e.g., Penning ionization). These new preliminary helium environment $G(H_2)$ values will be employed by *Task 3 - Sealed and Vented System Episodic Breathing and Gas Generation Prediction* to model the effect of radiolytic H_2 accumulation in helium environments to evaluate the practicality of extended storage in the DOE Standard Canister.

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ACRONYMS

ATR	Advanced Test Reactor
Al-1100	aluminum alloy 1100
ASNF	aluminum-clad spent nuclear fuel
DOE	Department of Energy
E_γ	gamma radiation energy
eV	electron volts
GC	gas chromatography
Gy min ⁻¹	Grays per minute
H ₂	molecular hydrogen
He*	helium excited state
He ^{•+}	ionized helium
HFIR	High Flux Isotope Reactor
INL	Idaho National Laboratory
kGy	kilo Gray
MeV	mega electron volts
$\tau_{1/2}$	half-life
°C	degrees Celsius
μL	microliter
$\mu\text{mol J}^{-1}$	micromoles per Joule

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1. INTRODUCTION

Aluminum-based alloys have been used as fuel cladding for a variety of nuclear reactors in the United States (U.S.) because of their low thermal neutron capture cross-sections, high thermal conductivity, and corrosion-resistant properties [1]. For example, the Idaho National Laboratory (INL) Advanced Test Reactor (ATR) and the Oak Ridge National Laboratory High Flux Isotope Reactor (HFIR) both employ aluminum-clad fuel elements. Consequently, the U.S. Department of Energy (DOE) is currently managing the storage of ~13 metric tons of aluminum-clad spent nuclear fuel (ASNF), and some of this ASNF will be placed in helium-backfilled canisters for extended (> 50 years) dry storage [2–4]. Assessment of this strategy is currently underway, and the amount of generation of radiolytic molecular hydrogen (H₂) is a key criterion of this evaluation.

The inherent ASNF radiation field promotes radiolysis of the surrounding environment, which, alongside the presence of hydrated aluminum oxyhydroxide corrosion layers (e.g., boehmite, gibbsite, and bayerite) on the cladding surface results in the formation of H₂ [5–13]. The generation of H₂ in the envisioned storage canister environment, though expected, is not ideal, as it may lead to pressurization and the formation of explosive and flammable gas mixtures. Consequently, an experimental research effort was initiated, as part of the “Technical Considerations and Challenges for Extended (> 50 years) Dry Storage of ASNF” program, to investigate the influence of several parameters (absorbed dose, extent of corrosion, gaseous environment, humidity, and temperature) on the radiolytic formation of H₂ from the gamma irradiation of aluminum coupons. This initiative (“Task 2 - Oxyhydroxide Layer Radiolytic Gas Generation Resolution”) demonstrated that the yield of H₂ increased with absorbed dose, pre-corrosion (versus pristine), humidity (up to ~50% relative humidity), and temperature [13]. Interestingly, H₂ formation was found to be sensitive to the gaseous environment (air, nitrogen, or argon) present during irradiation, as shown by Figure 1.

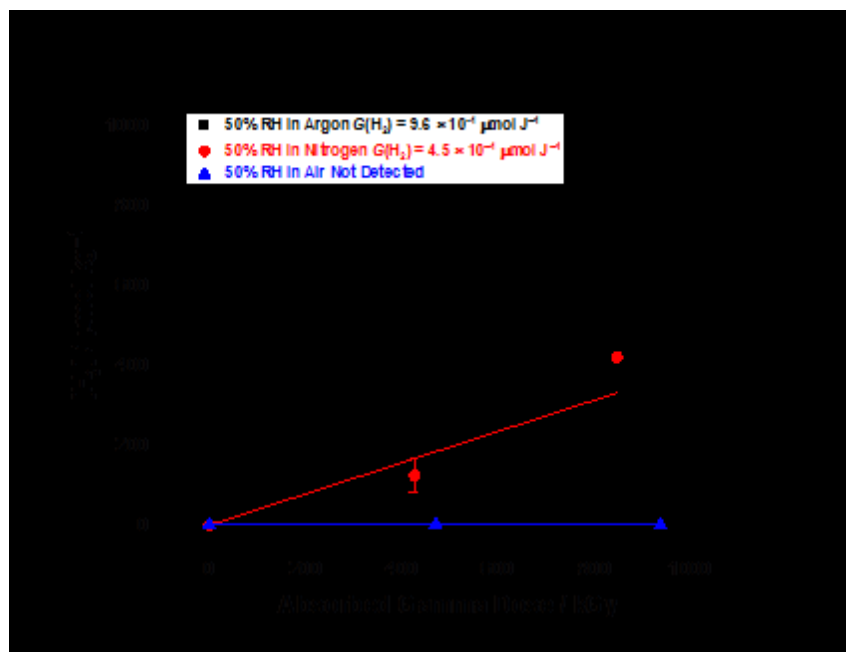


Figure 1. Concentration of H₂ (μmol kg⁻¹) measured after exposure of pre-corroded aluminum alloy 1100 coupons to gamma radiation (46 Gy min⁻¹) at ambient temperature at 50% relative humidity as a function of absorbed gamma dose: argon (●); nitrogen (●); and air (■) [13].

This study demonstrated that the highest radiolytic of H₂ yield was measured for the most chemically inert gaseous environment, argon. This observation was concerning as the current intention is for helium to be used as the back-fill gas for the standard DOE canister for the extended dry storage of ASNF. Helium is also a chemically inert gas but has a far greater first ionization energy than argon (24.59 eV versus 15.76 eV, respectively). The implication is that helium may promote the formation of a larger yield of H₂ than is currently accounted for by the program's complementary modeling component ("Task 3 - Sealed and Vented System Episodic Breathing and Gas Generation Prediction"), which may ultimately lead to the higher canister pressures than originally predicted [2–4].

To this end, we report preliminary H₂ data from the gamma irradiation of pristine and pre-corroded aluminum alloy 1100 (Al-1100) coupons in helium environments at ambient temperature at 0% and 50% relative humidity, to evaluate the impact of helium on radiolytic H₂ production.

2. EXPERIMENTAL METHODS

2.1 Materials

Aluminum alloy 1100 coupons (Al-1100, 2.5 cm 0.65 cm 0.15 cm) were purchased from Metals Samples Company - Alabama Specialty Products, Inc. Acetone (*HPLC Plus*, $\geq 99.9\%$) and ethanol (*absolute*, $\geq 99.8\%$) were supplied by MilliporeSigma. Helium was purchased in its highest available purity from Norco. Ultra-pure water (18.2 M Ω cm) was used for all water applications. All Al-1100 coupons were cleaned, weighed, pre-corroded, and weighed again as previously described [13].

2.2 Gamma Irradiations

Gamma irradiations were performed using the INL Center for Radiation Chemistry Research Foss Therapy Services Cobalt-60 Irradiator unit. Samples comprised individually flame-sealed glass ampules containing a single pristine or pre-corroded Al-1100 coupon in a helium gaseous environment at either 0% or 50% relative humidity. Samples were loaded in a bespoke multiposition sample holder and irradiated at ambient irradiator temperature ($\sim 45^\circ\text{C}$, as determined using a calibrated NI USB-TC01 Single Channel Temperature Input Device with K-type thermocouples) over several days to achieve the desired absorbed gamma doses. Dosimetry was determined for each sample position by Fricke solution [14,15] and corrected for the radioactive decay of cobalt-60 ($\tau_{1/2} = 5.27$ years; $E_{\gamma 1} = 1.17$ MeV and $E_{\gamma 2} = 1.33$ MeV) and aluminum electron density (0.8673) [13,16].

2.3 Gas Chromatography

An SRI 8610 model GC instrument equipped with a reduction gas detector (RGD) [17] was employed for all reported H₂ measurements and used in a "crush tube" configuration as previously described [18]. This method has an estimated error of $\leq 10\%$ and a H₂ sensitivity limit of 1 μL [18] and an upper detection limit of 20 μL . The yields of H₂ are reported in $\mu\text{mol kg}^{-1}$ of aluminum coupon and as radiation chemical yields—*G*-values—in SI units of $\mu\text{mol J}^{-1}$ (1 $\mu\text{mol J}^{-1} = 9.62$ (molecule 100 eV) $^{-1}$) as calculated from linear fits to data.

3. RESULTS AND DISCUSSION

The radiolytic formation of H₂ from the gamma irradiation of pristine and pre-corroded Al-1100 coupons in He environments is shown in Figure 2. The complete data set is given in Table 2 in Appendix A.

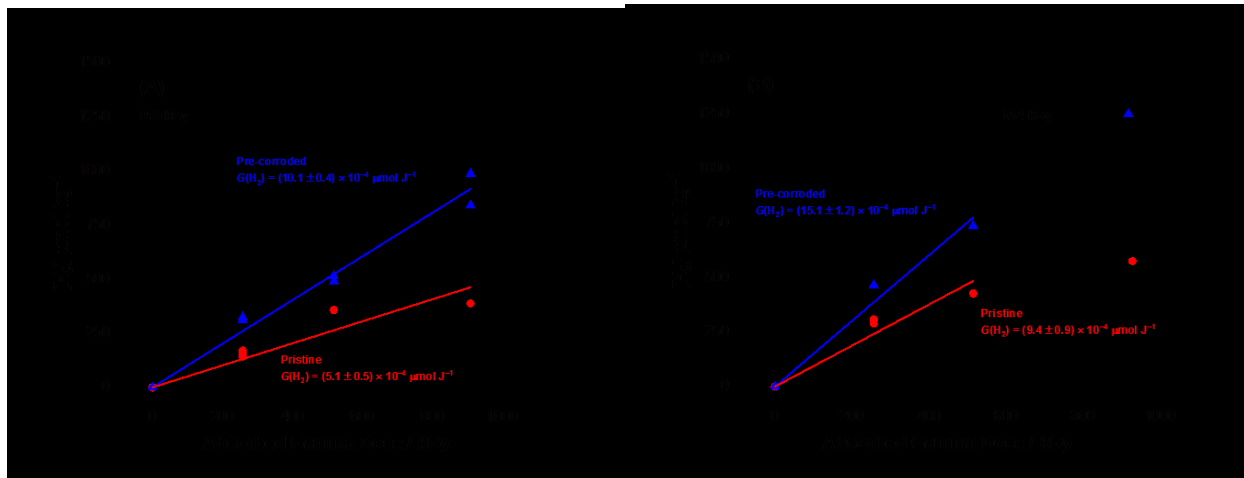
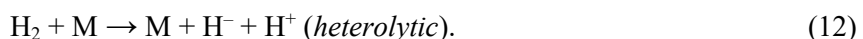
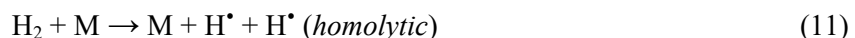


Figure 2. Concentration of H_2 ($\mu\text{mol kg}^{-1}$) as a function of absorbed gamma dose from the irradiation of pristine (●) and pre-corroded (■) aluminum alloy 1100 coupons in helium environments at 0% (A) and 50% (B) relative humidity at ambient irradiator temperature. Solid lines are linear fits to data for G -value calculation.

These trends are predominantly a consequence of radiolytic processes that occur at the Al-1100 coupon surface (M) following radiolytic production, diffusion, and reaction of excitons (h^+ and e^-). These reactions include the generation of H_2 via the oxidation of adsorbed water by hole transfer (h^+) and abstraction reactions, generalized by equations 1–7 [19–22]:



The concentration of H_2 increases linearly with absorbed gamma dose until a steady-state concentration is reached, at which point the precursors to H_2 are depleted and H_2 becomes progressively more involved in radiolytic processes (e.g., equations 8–10) and dissociation at the materials surface (equations 11–12 [23,24]):



Our previous nitrogen and argon environment studies were irradiated to doses up to 1.0 MGy, within which H_2 production exhibited a linear response to absorbed dose for all system permutations [13]. Here we were able to attain sufficiently high gamma doses (> 1.0 MGy) for H_2 production to deviate from linearity, as demonstrated by the pristine coupon data shown in Figure 2 (B) and Figure 3 in Appendix B, which is indicative of the amount of H_2 approaching a steady-state concentration. Although our pre-

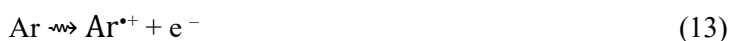
corroded coupons also exhibited deviation from linearity, these values were above our upper limit of detection (20 μL) and, as such, are not reported here. However, follow-up experiments, using an alternative GC method with a higher upper limit, are underway to further evaluate this deviation in H_2 yield for pre-corroded coupons. These steady-state observations are critical for the modeling component of the “Technical Considerations and Challenges for Extended (> 50 years) Dry Storage of ASNF” program, as G -values only provide an initial rate of species production, while steady-state data provide a means to evaluate the chemical reaction set employed by the model for the prediction of H_2 production over decades of accumulated dose.

Concerning the radiolytic yield of H_2 , irradiation of Al-1100 coupons in helium environments afforded higher yields of H_2 compared to the relatively high yields reported for complementary argon environments [13], as shown in Table 1.

Table 1. Comparison of H_2 G -values for gamma irradiated pristine and pre-corroded aluminum alloy 1100 coupons in argon and helium environments at 0% and 50% relative humidity. Argon G -values were sourced from [13]. Helium G -values were calculated from linear fits using H_2 data points $\leq 20 \mu\text{L}$.

Coupon state	Gaseous environment	Relative humidity (%)	$G(\text{H}_2)$ ($10^{-4} \mu\text{mol J}^{-1}$)
Pristine	Ar	0	3.6 ± 0.3
		50	7.3 ± 0.3
	He	0	5.1 ± 0.5
		50	9.4 ± 0.9
Pre-corroded	Ar	0	7.3 ± 0.8
		50	9.6 ± 0.6
	He	0	10.1 ± 0.4
		50	15.1 ± 1.2

Argon was shown to yield higher H_2 yields than both complementary air and nitrogen systems [13], which was attributed to the inability of argon to chemically interfere with radiolytic processes occurring at the material’s surface (e.g., equations 1–8) and directly decompose H_2 by charge transfer (equation 14):



owing to their similarity in first ionization energy: argon = 15.76 eV and H_2 = 15.4 eV [25]. The increase in $G(\text{H}_2)$ for helium environments ranged between 28% and 58%, relative to values for argon environments, Table 1. This enhancement is attributed to helium possessing a significantly higher first ionization energy (24.59 eV [25]) relative to argon. Consequently, less energy is expected to be transferred from the Al-1100 surface to a helium medium and is thus more available for promoting surface-mediated radiolytic processes. Further, any energy absorbed to a helium medium can be expected to be transferred to the Al-1100 surface, radiolytically generated species, and other molecules in the gas phase, by processes such as Penning ionization (Equations 15–16):



whereby the radiolytically generated excited states of helium (He^*) possess energies in excess of the ionization potential of chemical species they collide with, thereby inducing ionization via de-excitation of the He^* . This effect has been well characterized for ionization of several noble gases (Ar, Kr, and Xe), other small molecules (e.g., H_2 and CH_4), and some metals (e.g., Li and Na) by He^* [26–33]. This

particular process may also be the reason for the onset of a steady-state H₂ concentration at higher doses for pristine coupons in Figure 2 (B) and Figure 3 in Appendix B. Both ionized helium (He^{•+}) and He* have energies in sufficient excess of the ionization potential of H₂ to promote its decomposition via the proposed reactions below:



4. CONCLUSIONS

The purpose of this investigation was to evaluate the effect of helium gas on the radiolytic yield of H₂ from irradiated pristine and pre-corroded Al-1100 coupons, as helium has been proposed as the back-fill medium for the standard DOE canister for extended dry storage of ASNF. Here, we have demonstrated that helium gas promotes the radiolytic formation of greater yields of H₂, up to 58%, relative to previously investigated argon systems. Further, the presented data exhibit deviation from linearity with increasing dose, indicating the approach to a steady-state H₂ concentration, which is a critical value for evaluating complementary modeling efforts. Overall, the presented helium *G*-value data and dose dependence trends are useful as preliminary seeds for computer calculations, while follow-on helium studies are necessary and underway to evaluate this effect to higher doses.

5. ACKNOWLEDGMENTS

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Appendix A

Table 2. Complete preliminary helium environment H₂ data set from the irradiation of pristine and pre-corroded aluminum alloy 1100 coupons. *20 μ L is the detection limit for the employed analytical method, as detector saturation occurs above this value.

Coupon state	Relative humidity (%)	Absorbed gamma dose (kGy)	H ₂ volume (μ L)	G(H ₂) (μ mol J ⁻¹)
Pristine	1	258.36	2.22	0.00066
	1	258.36	2.00	0.00055
	1	258.36	2.07	0.00061
	1	518.86	4.74	0.00069
	1	909.83	5.49	0.00043
	2	1864.70	9.38	0.00033
	4	4977.29	16.62	0.00023
	47	256.33	4.36	0.00120
	47	256.33	4.37	0.000113
	46	514.53	6.08	0.00083
	47	927.89	8.64	0.00062
Corroded	2	258.36	5.31	0.00126
	2	258.36	5.10	0.00120
	2	518.86	8.67	0.00099
	2	518.86	8.14	0.00095
	2	909.83	14.21	0.00093
	2	909.83	16.41	0.00109
	2	1864.70	< 20*	-*
	2	4641.10	< 20*	-*
	51	256.33	7.88	0.00182
	53	514.53	12.53	0.00143
	52	917.20	20.66	0.00136

APPENDIX B

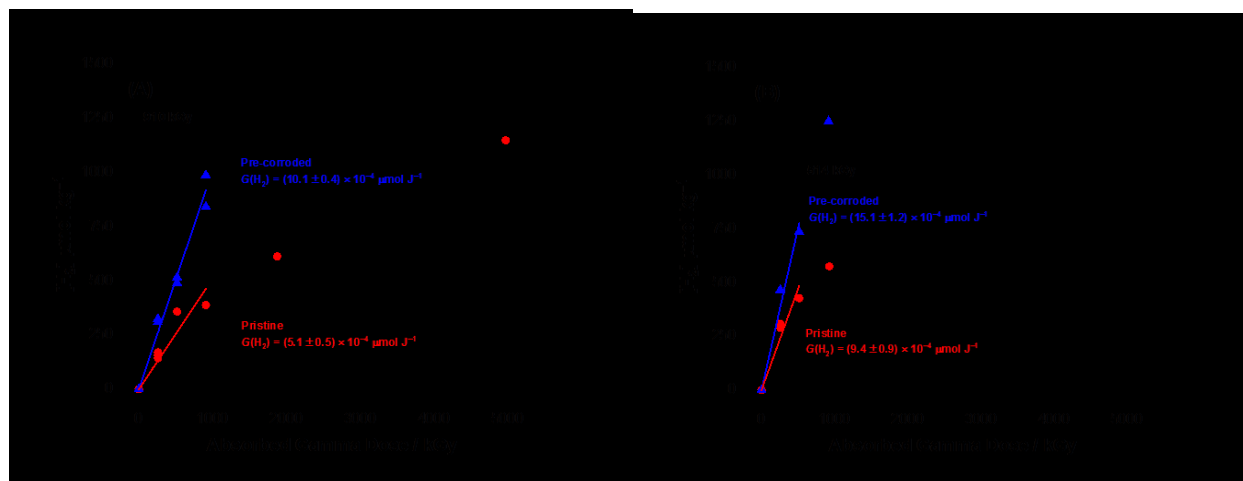


Figure 3. Complete data set for the concentration of H_2 ($\mu\text{mol kg}^{-1}$) as a function of absorbed gamma dose from the irradiation of pristine (●) and pre-corroded (■) aluminum alloy 1100 coupons in helium environments at 0% (A) and 50% (B) relative humidity at ambient irradiator temperature. Solid lines are linear fits to data for G -value calculation.