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Chemistry Research

Task 2: Radiolytic Gas Generation due to ASNF Corrosion Layers

LRS Number: INL/MIS-21-63682 Rev:000

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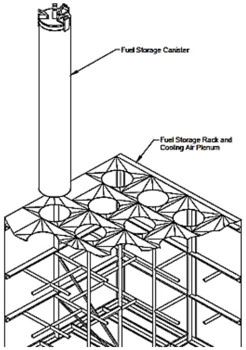
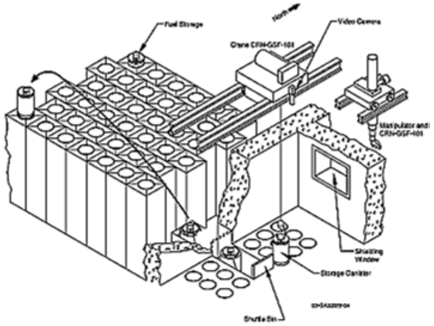
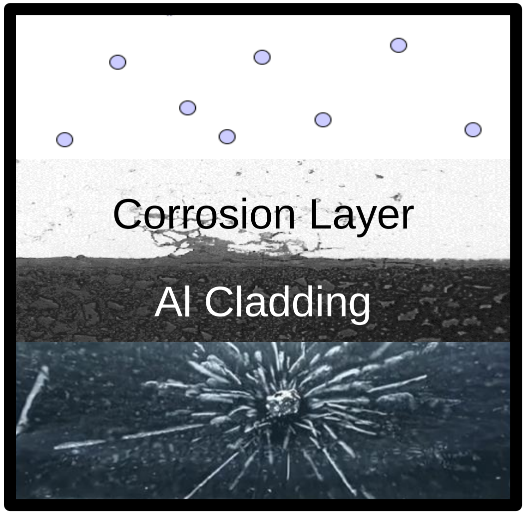
INL Idaho National Laboratory

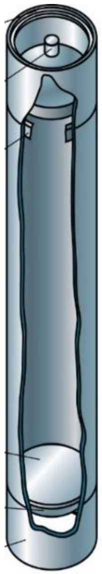
Radiolytic Gas Generation due to ASNF Corrosion Layers

- Thermal and chemical corrosion of *Aluminum-clad Spent Nuclear Fuel* (ASNF) is well understood.
- Radiation-induced **H_2** gas generation from the attendant Al corrosion layer(s) is less understood for ASNF.
- Radiolytic generation of **H_2** from solid and gaseous sources presents potential challenges for the long-term storage of ASNF (>50 years) in the form of:
  - **over pressurization**
  - **cladding embrittlement**
  - **formation of flammable gas mixtures**









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Radiation-Induced H_2 Production Pathways

Water Radiolysis

$$H_2O \rightsquigarrow e_{aq}^-, H^\bullet, {}^\bullet OH, H_2, H_2O_2, H_{aq}^+$$

Surface Processes

$$Al_{(s)} \rightsquigarrow h^+ + e^-$$

Water Processes

$$H_2O^* \rightarrow H_2 + O$$

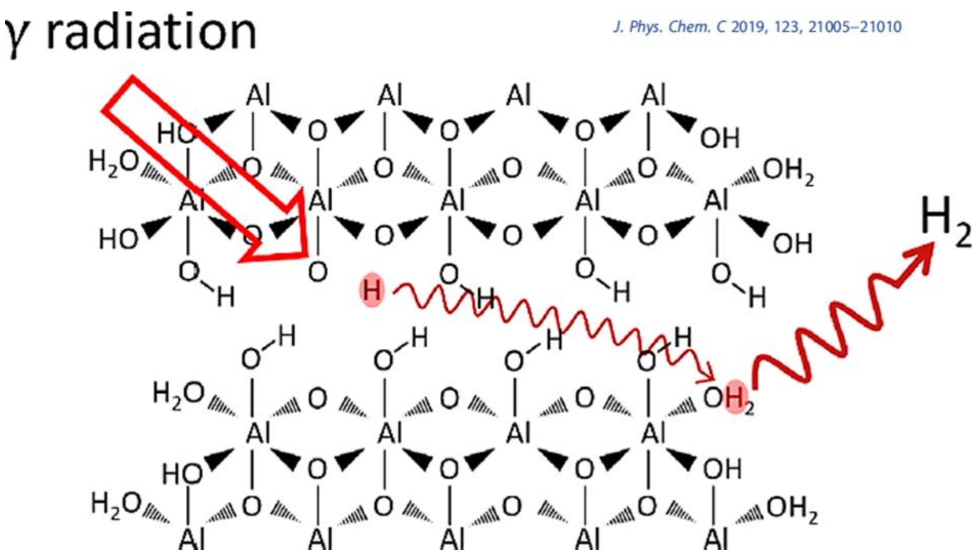
$$e_{aq}^- + e_{aq}^- + 2H_2O \rightarrow H_2 + 2OH^-$$

$$e_{aq}^- + H^\bullet + H_2O \rightarrow H_2 + OH^-$$

$$e_{aq}^- + H_{aq}^+ \rightarrow H^\bullet$$

$$H^\bullet + H_2O \rightarrow H_2 + {}^\bullet OH$$

$$H^\bullet + H^\bullet \rightarrow H_2$$



J. Phys. Chem. C 2019, 123, 21005–21010

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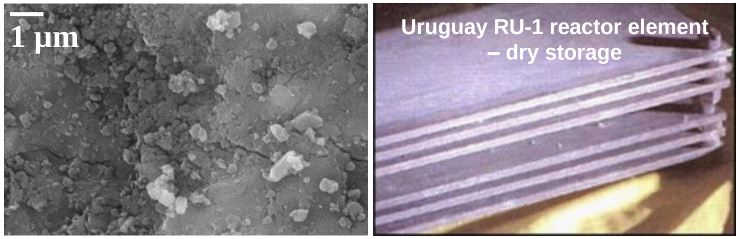
Task 2 Research Goal

Aim

- Provide quantitative experimental data and insight into the rate of H_2 generation from the attendant corrosion layer on aluminum alloy coupons to inform complimentary modelling efforts.

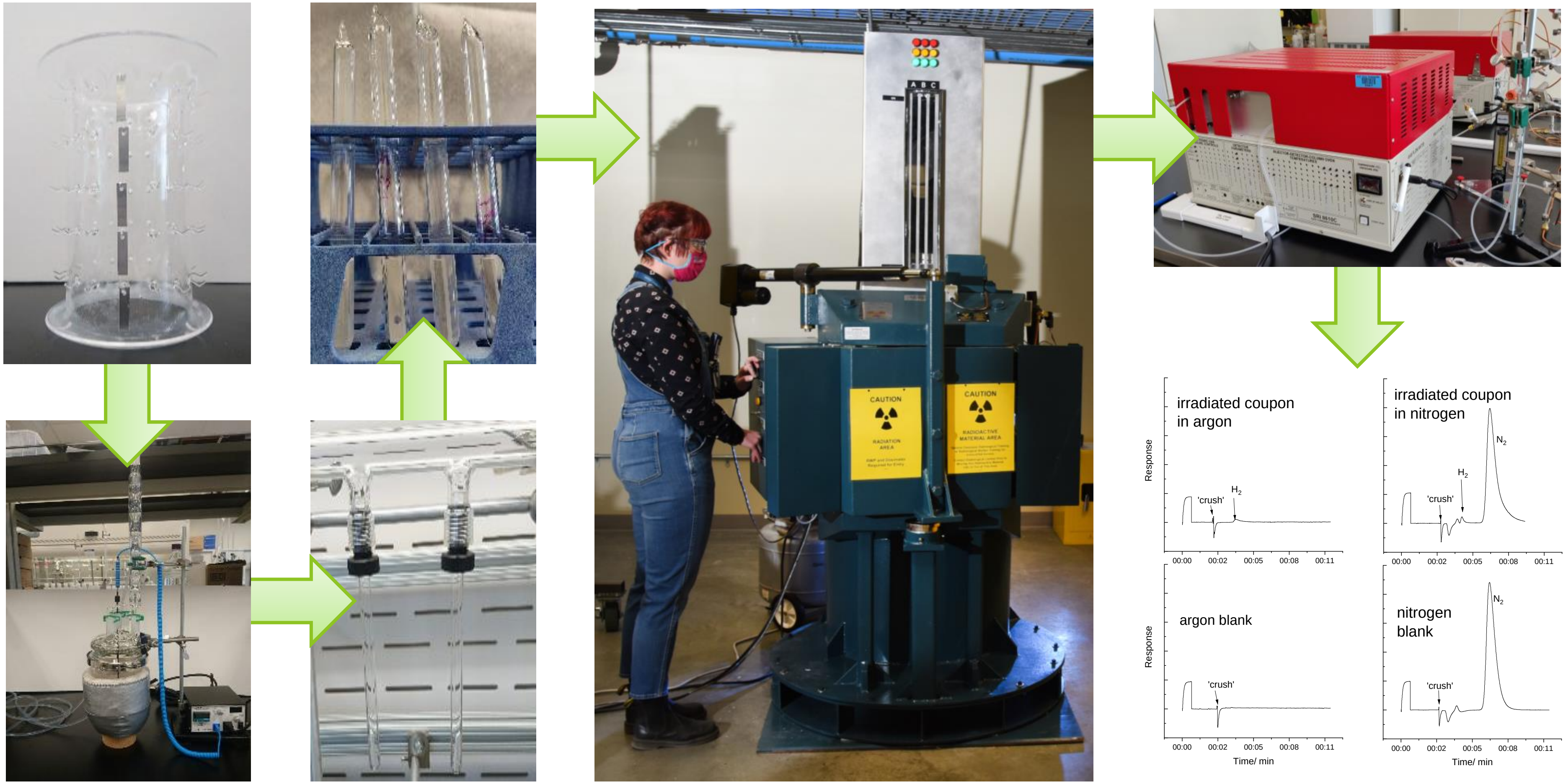
Objectives

- Evaluate radiation-induced H_2 generation as a function of:
  - **absorbed gamma dose**
  - **corrosion layer composition**
  - **gaseous environment**
  - **relative humidity**
  - **temperature**



RU-1 (Al-1100): 8 years in-reactor at ~70°C; ~30 years dry storage; 0.2-25 µm thick corrosion layer of gibbsite (P) and possibly boehmite (S).

Experimental Methodology



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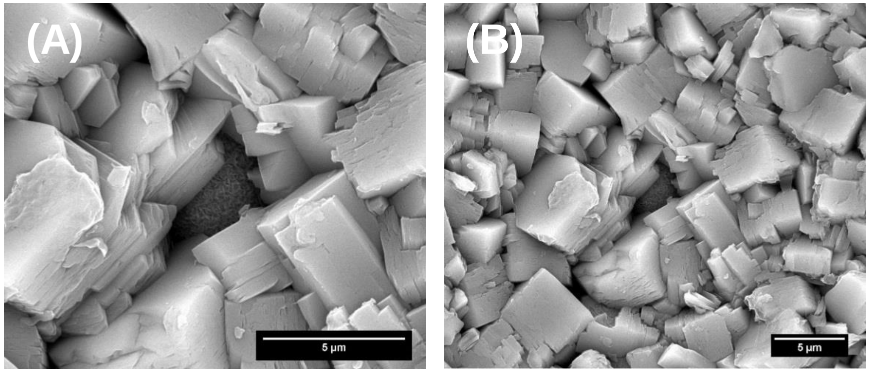
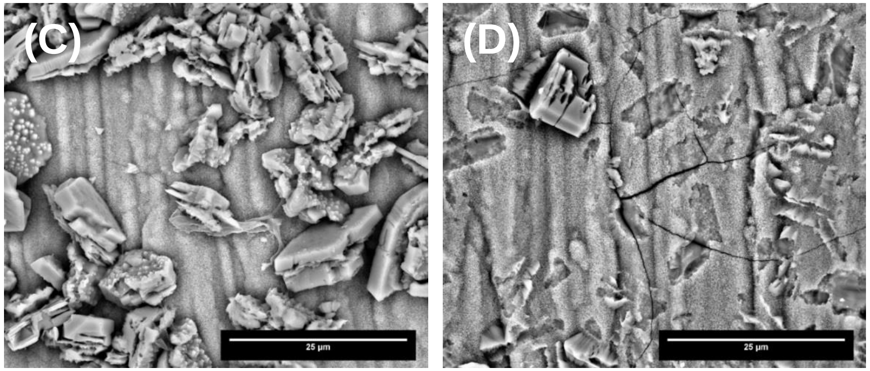
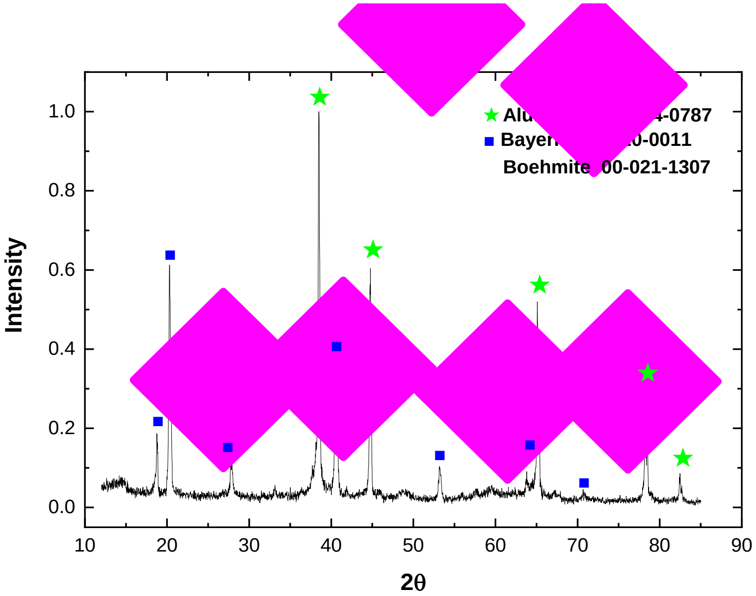
Corrosion Layer Composition

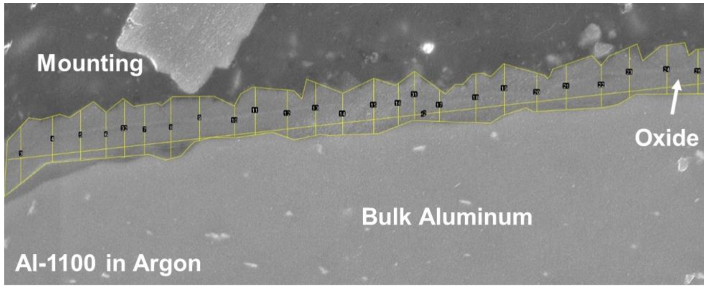
Non-Irradiated



H_3PO_4 Acid Strip







Average corrosion layer thickness of 5.3 ± 0.3 µm.

- Parker-Quaife, E.H.; Verst, C.; Heathman, C.R.; Zalupski, P.Z.; **Horne, G.P.**, *Radiation Physics and Chemistry*, **2020**, *177*, 109117.
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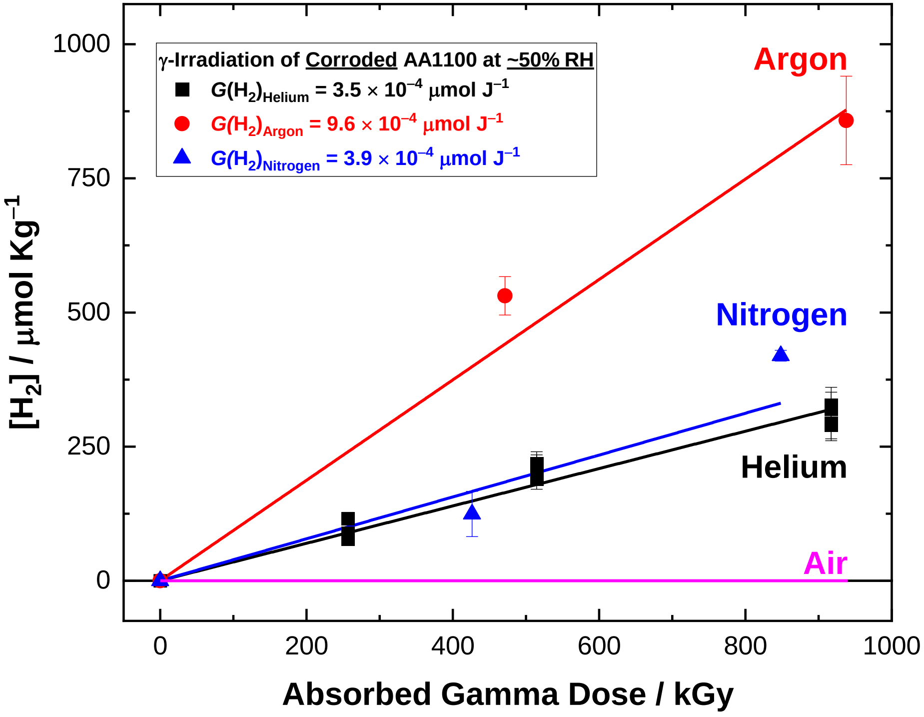
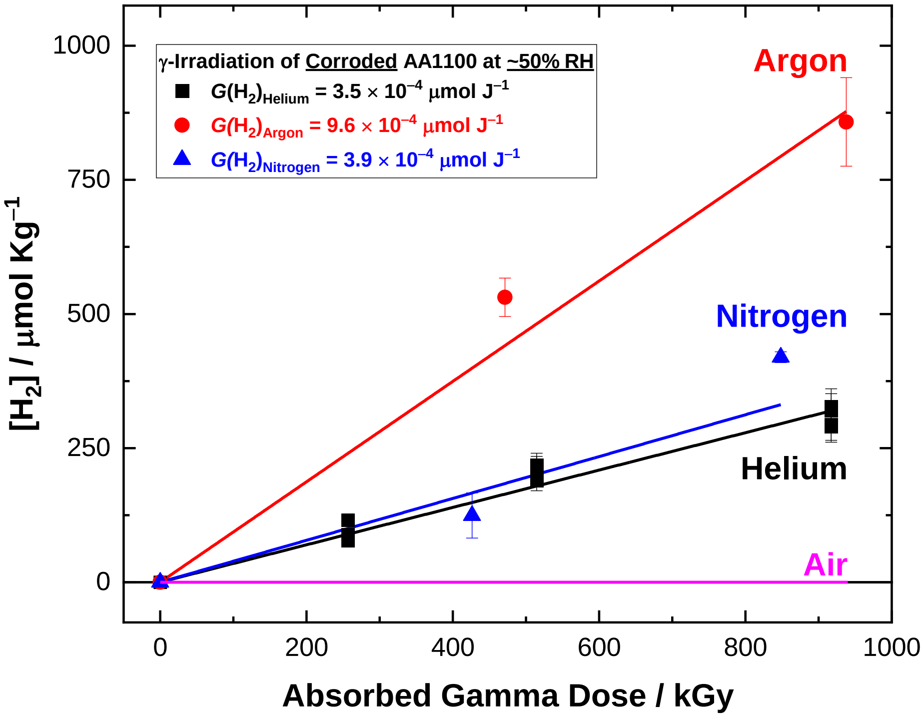
Absorbed Gamma Dose Dependence



- The volume of **H_2** increased with absorbed gamma dose.
- No **H_2** was detected in the absence of a AA1100 coupon at any investigated humidity (0%, 50%, and 100%).

- Parker-Quaife, E.H.; Verst, C.; Heathman, C.R.; Zalupski, P.Z.; **Horne, G.P.**, *Radiation Physics and Chemistry*, **2020**, *177*, 109117.

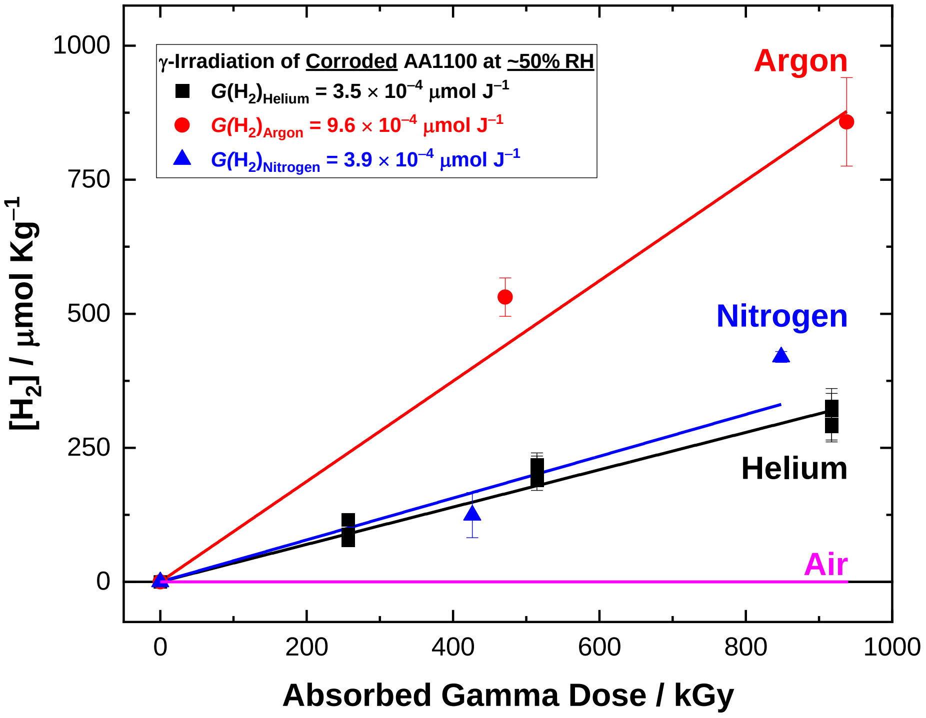
Gaseous Environment Dependence



- No H_2 was quantified in the presence of **Air**, O_2 scavenges radicals (e.g., e_{aq}^{-} and $H^{\bullet}$).
- **Nitrogen** and **Helium** play a minor role in H_2 inhibition, attributed to gas phase radical processes.

- Parker-Quaife, E.H.; Verst, C.; Heathman, C.R.; Zalupski, P.Z.; **Horne, G.P.**, *Radiation Physics and Chemistry*, **2020**, *177*, 109117.

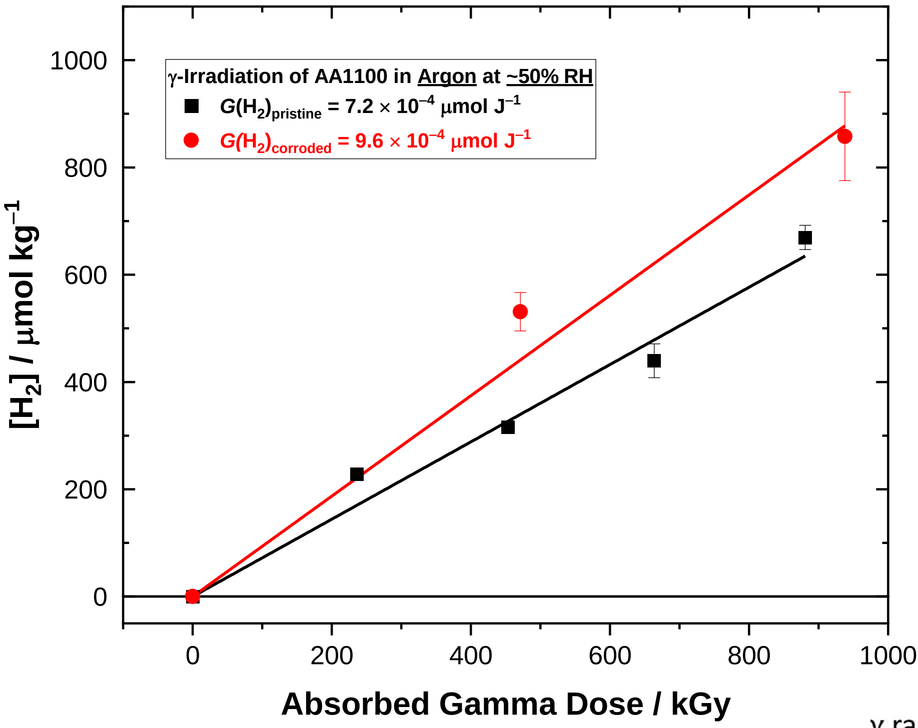
Gaseous Environment Dependence

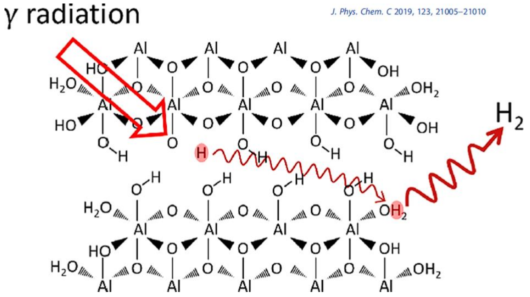


- For example, irradiation of **He** atmospheres promotes ***Penning Ionization***: $He^* + H_2 \rightarrow He + H_2^+ + e^-$.
- **Argon** affords the highest yield of H_2 as its ionization potential is "*just right*" (E^o_{Argon} = 15.76 V *vs*. E^o_{H2} = 15.4 V).

- Parker-Quaife, E.H.; Verst, C.; Heathman, C.R.; Zalupski, P.Z.; **Horne, G.P.**, *Radiation Physics and Chemistry*, **2020**, *177*, 109117.

Oxyhydroxide Corrosion Layer Dependence





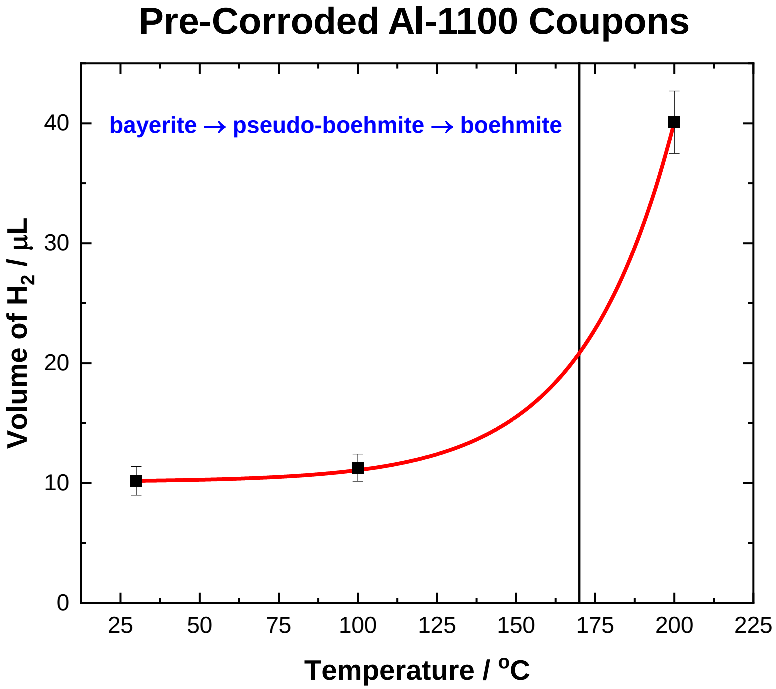
J. Phys. Chem. C 2019, 123, 21005–21010

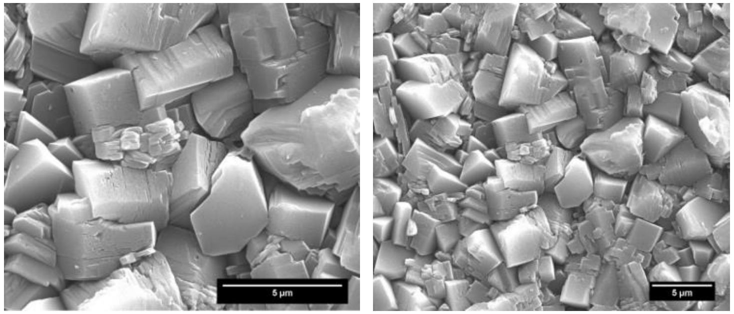
- Corrosion-induced oxyhydroxide layers provide >OH_2/>OH^-/>OH groups for promotion of H_2 formation.

- Parker-Quaife, E.H.; Verst, C.; Heathman, C.R.; Zalupski, P.Z.; **Horne, G.P.**, *Radiation Physics and Chemistry*, **2020**, *177*, 109117.

Temperature Dependence

- Irradiation at 100 °C gave H_2 yields similar to ambient temperature values.
- Irradiation at 200 °C showed a significant increase (3-4-fold) in H_2 production.
- A combination of temperature-driven phenomena may be responsible for the higher yield of H_2 at 200 °C:
  - **phase transformation of corrosion layers starting at ~170 °C.**
  - **more efficient release of $H^\bullet$ and H_2 from boehmite layers**





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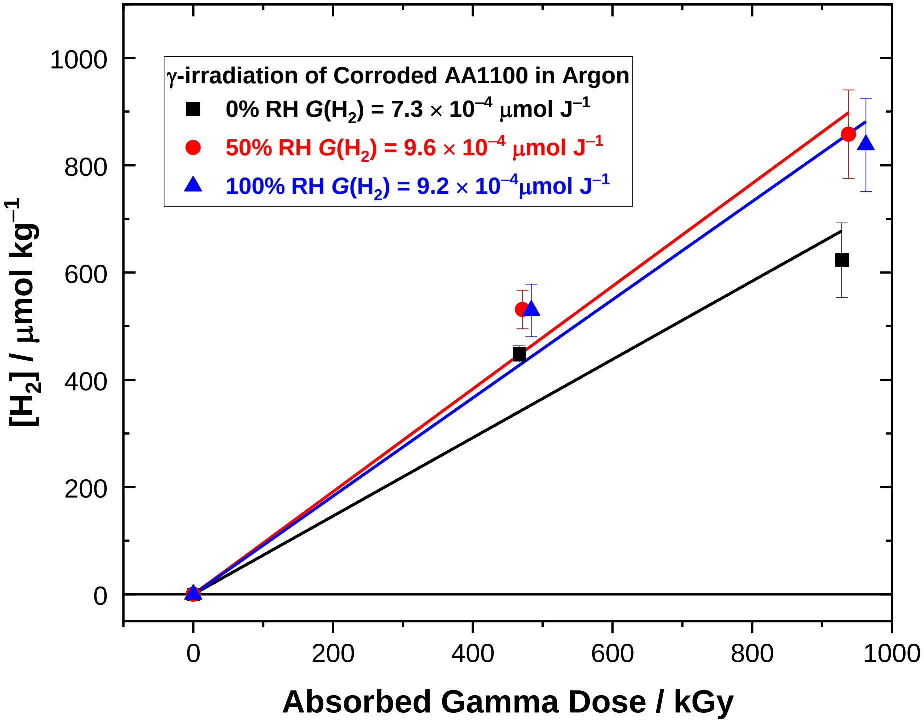
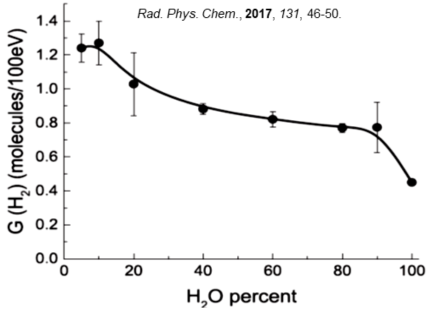
Humidity Dependence



- Higher H_2 yields with increasing relative humidity.
- Direct water radiolysis and energy migration from the irradiated coupon to surface bound water molecules.



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- J.A. LaVerne and P.L. Huestis, *J. Phys. Chem. C*, 2019, **123**, 21005.

Conclusions

1. Radiation promotes H_2 formation from AA1100 coupons.
2. $G(H_2)$ is dependent on *gaseous environment*, *temperature, humidity*, and *presence of a corrosion layer*.
3. This work has generated a series of $G(H_2)$ values to support predictive model development.

Future Research Questions

1. How does corrosion layer surface composition change with absorbed dose upon reaching steady-state?
2. What effect does alloy composition have on H_2 production?

materials

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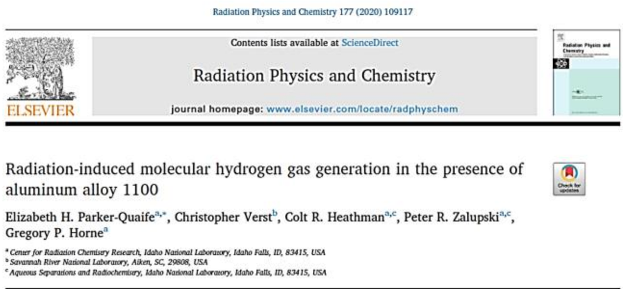

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Radiation-induced molecular hydrogen gas generation in the presence of aluminum alloy 1100

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[b] Savannah River National Laboratory, Aiken, SC, 29808, USA
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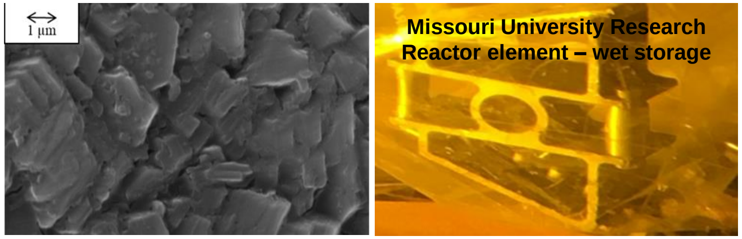
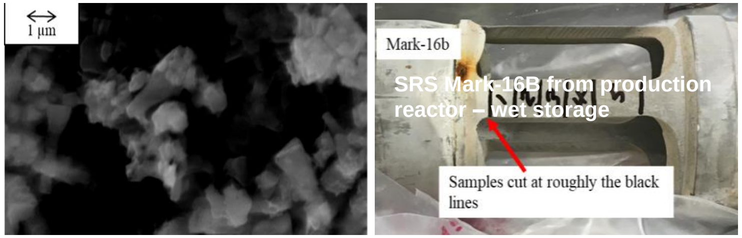


MURR (<u>Al-6061</u>): ~113 days in-reactor at ≥ 60°C; <18 years wet storage at ~22°C; 5-10 µm thick corrosion layer of bayerite (P) and boehmite (S).



Mk-16b (<u>Al-6061</u> or <u>Al-6063</u>): ~220 days in-reactor at ≥ 34 °C; ~40 years wet storage at ~22°C; 5-15 µm thick corrosion layer of bayerite (P), boehmite (S), and gibbsite (T).

Acknowledgements

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Center for Radiation Chemistry Research

Summary of Project Deliverables (FY19-20)

1. **Milestone 2.6:** Complete Round-Robin Hydrogen Gas Analysis Capability Comparison. Technical report, DOI: https://doi.org/10.2172/1755761.
2. **Milestone 2.7:** Evaluation of Techniques for the Measurement of Molecular Hydrogen Gas in Helium Matrices. Technical report.
3. **Milestone 2.8:** *Preliminary Radiolytic Gas Generation Measurements from Helium-Backfilled Samples*. Technical report, DOI: https://doi.org/10.2172/1768757.
4. Parker-Quaife *et al.*, *Rad. Phys. Chem.*, **2020**, *177*, 109117, DOI: https://doi.org/10.1016/j.radphyschem.2020.109117.

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ABSTRACT

The United States government currently manages nearly 13 metric tons of aluminum-clad spent nuclear fuel (SNF) without a long-term storage solution, so a fundamental understanding of corrosion processes occurring on aluminum alloy surfaces is of utmost importance to plan for extended (> 50 years) interim dry storage of aluminum-clad SNF. While thermal and chemical corrosion processes are well characterized for aluminum, radiation effects are not. To help understand the impacts of radiation on aluminum-clad SNF, the radiation-induced molecular hydrogen gas (H_2) generation from pristine and pre-corroded aluminum alloy 1100 (Al-1100) coupons has been studied. Corrosion of coupons was achieved by submerging coupons in water at 95 °C for 29 days, yielding a ~5 µm boehmite/bayerite oxide film. Pre-corroded coupons were exposed to cobalt-60 gamma radiation to absorbed doses of up to 1.0 MGy under a variety of conditions: cover-gas composition (argon, nitrogen, or air), relative humidity (0, 50, and 100%), and temperature (ambient, 100, and 200 °C). Post-irradiation measurements demonstrated that the yield of H_2 was directly attributable to the presence of the Al-1100 coupons and their physisorbed water with dependence on absorbed gamma dose, relative humidity, and cover-gas composition. No H_2 was quantified in the presence of air, while both nitrogen and argon environments afforded higher H_2 yields with increasing relative humidities. This was attributed to the greater availability of adsorbed water for radiolytic processes. Irradiation of pre-corroded Al-1100 coupons at different temperatures under 0% relative humidity argon conditions yielded statistically equivalent H_2 yields for ambient temperatures and 100 °C. However, irradiation at 200 °C promoted a 3 to 4-fold increase in the yield of H_2, possibly due to the transformation of bayerite to boehmite and/or improved efficiency of $H^•$ and H_2 release from oxide surfaces.

1. Introduction

Owing to their corrosion resistance, high thermal conductivity, and low thermal neutron capture cross-section properties, aluminum-based alloys (e.g., 6061, 1100, and SZAV-1) have been utilized as nuclear fuel cladding for a wide-spectrum of reactor types often found at universities and research institutes, including the Idaho National Laboratory (INL) Advanced Test Reactor (ATR), the Oak Ridge National Laboratory (ORNL) High Flux Isotope Reactor (HFIR), and smaller Training Research Isotopes General Atomics (TRIGA) reactors (Corrosion of Research Rea, 2009; Kim et al., 2008). In-reactor service exposes these aluminum alloys to extreme environments: high temperatures, immersion in chemically treated moderators and coolants, and an intense multi-component radiation field (alpha and beta particles, gamma and X-rays, neutrons, and fission fragments), all ultimately leading to various forms of corrosion (e.g., pitting, crevice, galvanic, and intergranular) (Corrosion of Research Rea, 2009; Kim et al., 2008). Follow-on wet storage in cooling ponds promotes further aluminum corrosion chemistry and continued radiation exposure from its radioactive contents. As corrosion penetrates the aluminum cladding, the integrity and release of highly radioactive Spent Nuclear Fuel (SNF) becomes a concern when considering extended storage. Corrosion processes negatively influence the physical and chemical properties of the aluminum cladding through the formation of aluminum hydroxide/oxyhydroxide hydrate layers. These layers contribute to radiolytic processes resulting in molecular hydrogen gas (H_2) generation (Elliot and Bartels, 2009; Hu, 2012; Wittman, 2013; Wittman and Hanson, 2015), which may lead to pressurization (Bonin et al., 2000)

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