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Chemistry Research

Task 2: Radiolytic Gas Generation due to ASNF Corrosion Layers

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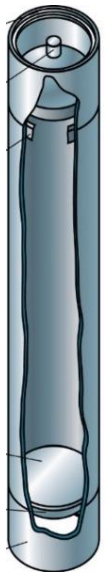
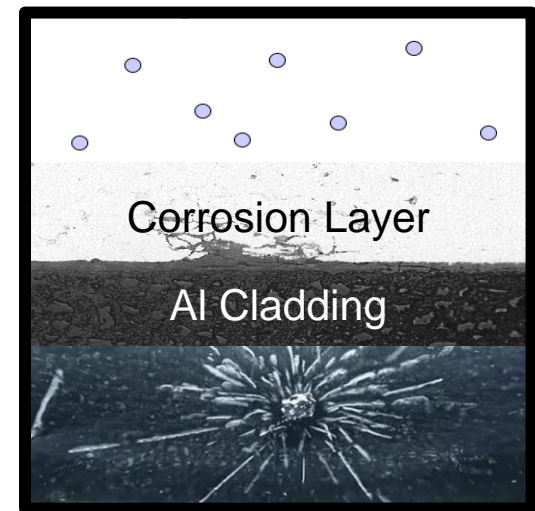
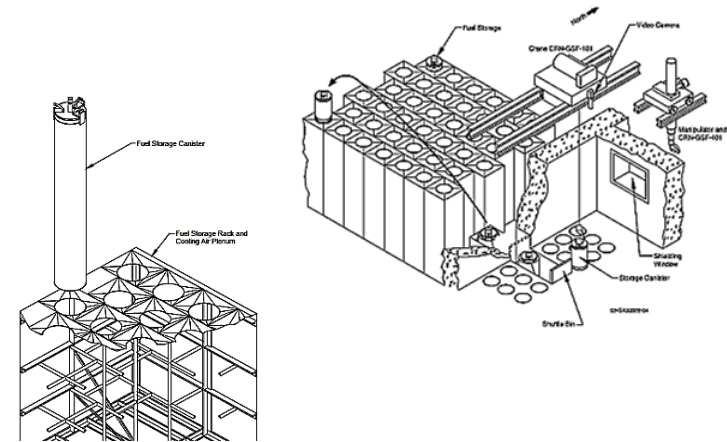
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Radiolytic Gas Generation due to ASNF Corrosion Layers

- 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

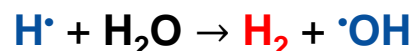
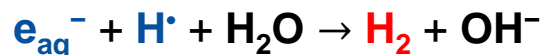
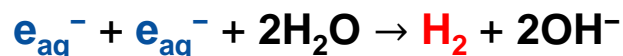
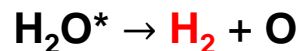


Radiation-Induced H₂ Production Pathways

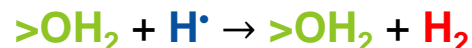
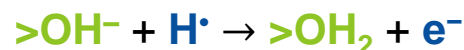
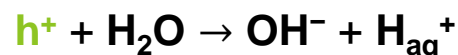
Water Radiolysis



Water Processes

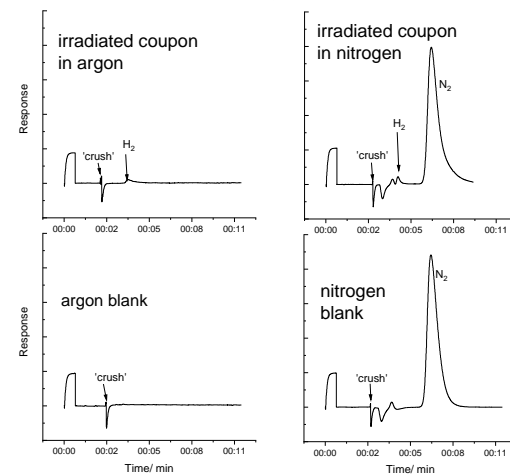
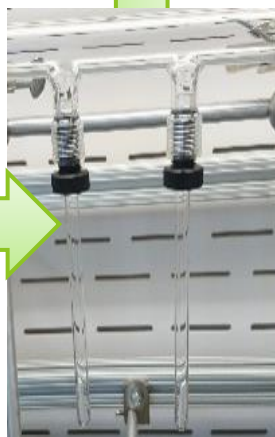
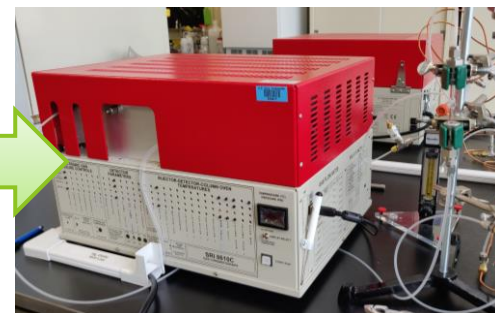


Surface Processes



- G.V. Buxton, C.L. Greenstock, W. Helman, and A.B. Ross, *J. Phys. Chem. Ref. Data*, 1988, **17**, 513.
- B.H. Milosavljevic and J.K. Thomas, *J. Phys. Chem. B*, 2003, **107**, 11907.
- J.K. Thomas, *Chem. Rev.*, 2005, **105**, 1683.
- J.A. LaVerne and P.L. Huestis, *J. Phys. Chem. C*, 2019, **123** (34), 21005.

Experimental Methodology



- J.A. LaVerne and R.H. Schuler, *J. Phys. Chem.*, 1984, **88** (6), 1200.
- J.A. LaVerne and P.L. Huestis, *J. Phys. Chem. C*, 2019, **123** (34), 21005.
- T.E. Lister, Vapor Phase Corrosion Testing of Pretreated Al1100, INL/EXT-18-52249, 2018.
- C. Vargel, Chapter B.1 - Introduction to The Corrosion of Aluminium in Vargel, C. (Eds.), *Corrosion of Aluminium*, Elsevier, 2004.

Key Findings

- H_2 yield increased with γ -dose. No H_2 without coupon.
- Higher H_2 yields were attained from pre-corroded coupons in Ar .
- Corrosion-induced oxyhydroxide layers provide $>\text{OH}^-$ groups for promotion of H_2 formation.
- No H_2 was quantified in the presence of air, O_2 scavenges radicals (e_{aq}^- and H^\cdot).
- N_2 plays a minor role in H_2 inhibition, attributed to gas phase radical processes.
- The highest H_2 yields were measured in Ar , attributed to its high first ionization energy (15.76 eV), preventing direct removal of H_2 .

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

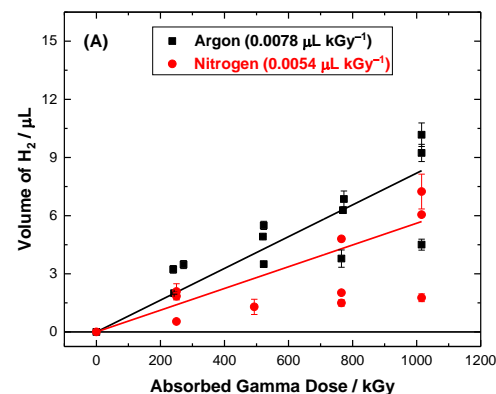
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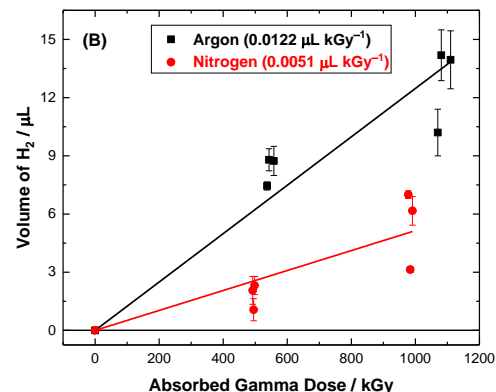
^b Savannah River National Laboratory, Aiken, SC, 29806, USA

^c Argonne Separations and Radiochemistry, Idaho National Laboratory, Idaho Falls, ID, 83415, USA

Pristine Al-1100 Coupons



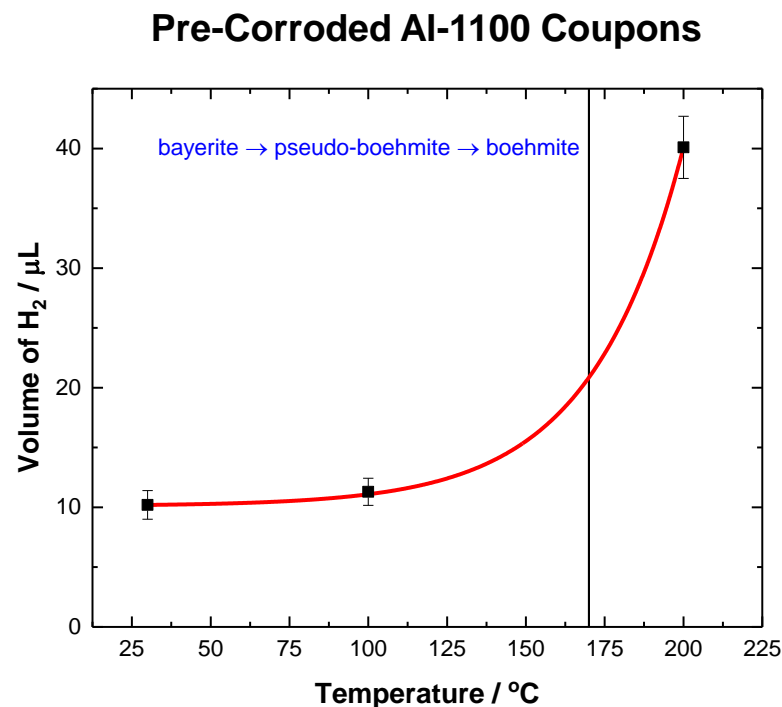
Pre-Corroded Al-1100 Coupons



- A. Russell Jones, *Rad. Res.*, 1959, **10**, 655.
- K. Karasawa, E. Ibe, S. Uchida, Y. Etoh, and T. Yasuda, *Rad. Phys. Chem.*, 1991, **37** (20), 193.
- D.T. Reed and R.A. Van Konynenburg, MRS Online Proceedings Library Archive 112, 1987.
- G. Clifton, *Physical Review*, 1920, **16.1**, 41.

Radiolytic H₂ Production vs. Temperature

- Gamma irradiation at 100 °C afforded H₂ yields statistically equivalent to those measured at ambient temperature.
- Irradiation at 200 °C showed a significant increase (3-4-fold) in H₂ production.
- A combination of temperature-driven phenomena may be responsible for the higher yield of H₂ at 200 °C:
 - **phase transformation of corrosion layers starting at ~170 °C.**
 - **more efficient release of H[•] and H₂ from boehmite layers**

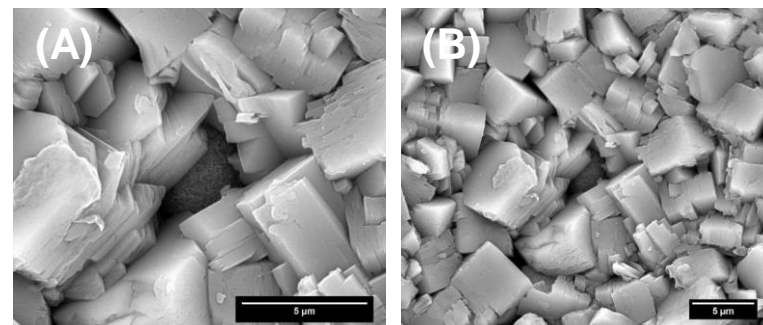
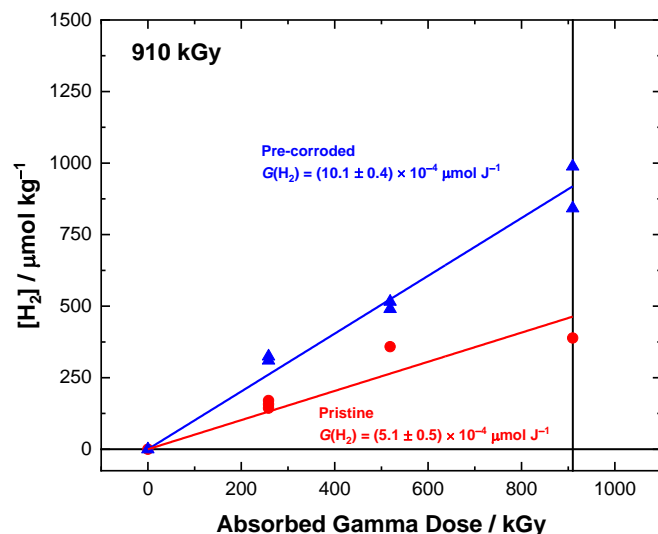


Current Research

1. Irradiation in **He** atmospheres – **Penning Ionization**:



2. Effect of alloy composition.
3. Surface characterization.



Element	Al-1100 (%)	Al-6061 (%)
Aluminum	99.00-99.95	95.85-98.56
Chromium	-	0.04-0.35
Copper	0.05-0.20	0.15-0.40
Iron	0.95	0.0-0.7
Magnesium	0.0	0.8-1.2
Manganese	0.05	0.0-0.15
Silicon	0.95	0.40-0.80
Titanium	-	0.0-0.25
Zinc	0.1	0.0-0.15
Residuals	0.15	0.15

- K.L. Bell, A. Dalgarno, and A.E. Kingston, A.E., *J. Phys. B (Proc. Phys. Soc.)*, 1968, **2** (1), 18.
- P. Huestis, C.L. Pearce, X. Zhang, X.A.T N'Diaye, K.M. Rosso, and J.A. LaVerne, *J. Nucl. Mat.*, 2018, **501**, 224.

Acknowledgements



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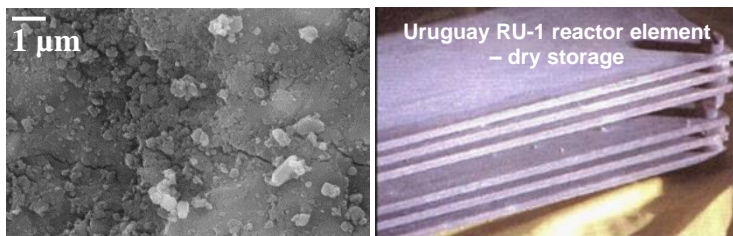
Project Deliverables (FY19-20)

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>.

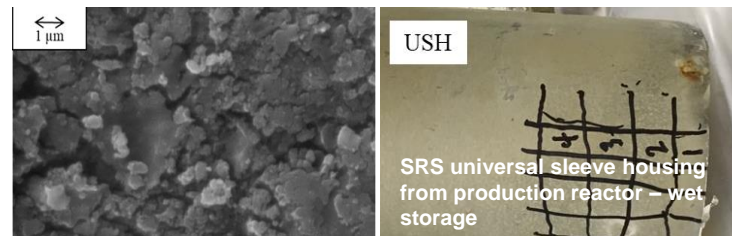




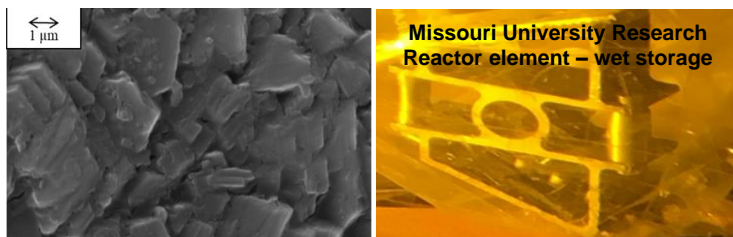
Surface Characterization of Stored ASNF



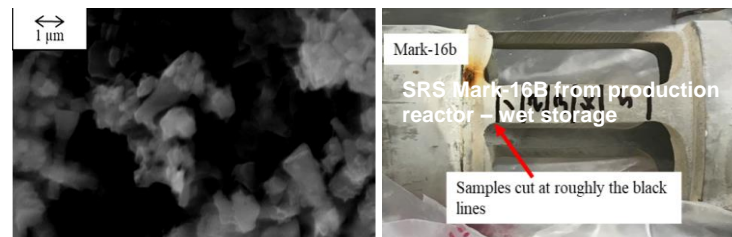
RU-1 (AI-1100): 8 years in-reactor at $\sim 70^{\circ}\text{C}$; ~ 30 years dry storage; 0.2-25 μm thick corrosion layer of gibbsite (P) and possibly boehmite (S).



USH (AI-6063): ~ 1800 days in-reactor at $\leq 93^{\circ}\text{C}$; ~ 40 years wet storage at $\sim 22^{\circ}\text{C}$; dense corrosion layer boehmite (P) and bayerite (S), thickness undetectable.



MURR (AI-6061): ~ 113 days in-reactor at $\geq 60^{\circ}\text{C}$; < 18 years wet storage at $\sim 22^{\circ}\text{C}$; 5-10 μm thick corrosion layer of bayerite (P) and boehmite (S).



Mk-16b (AI-6061 or AI-6063): ~ 220 days in-reactor at $\geq 34^{\circ}\text{C}$; ~ 40 years wet storage at $\sim 22^{\circ}\text{C}$; 5-15 μm thick corrosion layer of bayerite (P), boehmite (S), and gibbsite (T).