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Scale-Up Radiolysis Testing of Aluminum-clad SNF and Surrogates in a Mini-Canister Environment (part of Task 6)

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Radiolytic hydrogen generation

- Aluminum oxyhydroxides form on aluminum exposed to water
  - On fuel cladding during pre-treatments, in-reactor, and/or storage
  - Types
    - *Bayerite or gibbsite, $Al(OH)_3$ or $Al_2O_3{\cdot}3H_2O$, forms at low temperature (<80°C)*
    - *Boehmite, AlOOH or $Al_2O_3{\cdot}H_2O$, forms at higher temperature*
- Hydrogen (H_2) gas can be generated in dry storage canisters for aluminum-clad spent nuclear fuel (SNF) due to radiolysis of
  - Residual liquid water/water vapor
  - Physisorbed water
  - Aluminum oxyhydroxides (chemisorbed water)
- Potential for pressurization or flammable gas mixture
- Expected yield and rate of production needed for performance prediction and the safety basis

Mini-canister radiolysis testing

- Measure radiolytic gas generation in canister-analogous environment
  - Stainless-steel vessel
  - Helium cover gas (25 psia)
  - Lab-grown surrogates or reactor-exposed aluminum samples bearing Al oxyhydroxides
- On-line monitoring (multiple measurements over time for same test)
- Test data used to
  - Evaluate impact of drying
  - Benchmark models

- Commercial small canisters
- Gas sampling ports on top connect to instrumentation

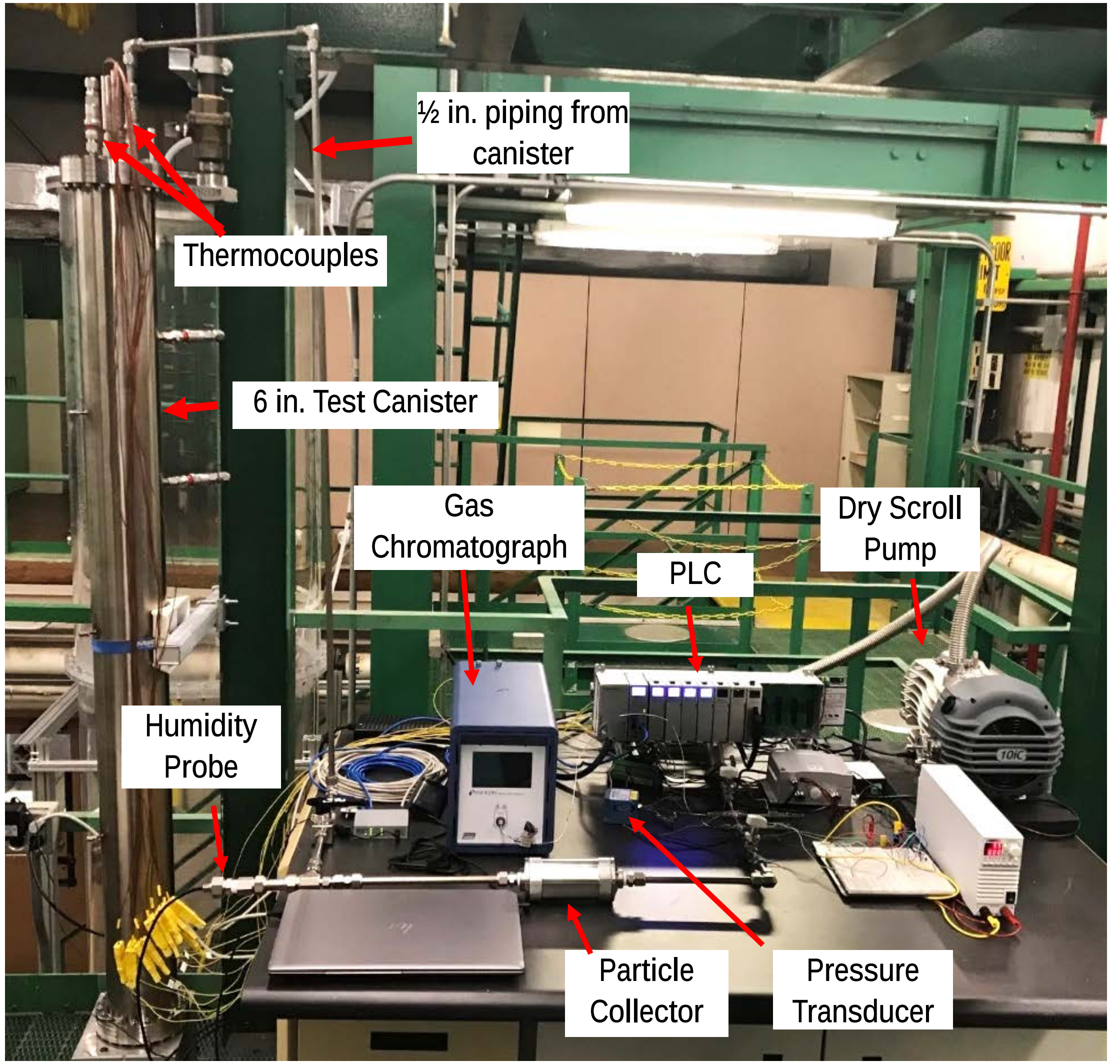
Loaded and sealed mini-canister with reactor-exposed sample

- Tested in Co-60 (gamma) irradiator
  - Stand-in for spent fuel environment
  - Dose rate for samples: 37.8 krad/hr (gamma)
  - Ambient irradiator temperature: ~23.5°C
- Gas sampled at intervals during test
- Gas monitoring system
  - Two-column gas chromatograph: Ar and He carrier gases
  - 20-m Ar column for greater separation of H_2 from He cover gas
  - H_2 sensitivity down to 100 ppm
  - N_2 and O_2 sensitivity down to 20 ppm

On-line monitoring instrumentation

- System developed for future monitoring of an actual ASNF dry storage “demo” canister

- Instrumentation
  - Valves, tubing, and vacuum pump to withdraw sample
  - Particle collector to capture particulates
  - Ion chamber to measure radioactivity in exiting gas
  - Gas characterization
    - *Humidity sensor*
    - *Gas chromatograph*
    - *Pressure transducer*
  - He tank for optional topping off He
  - HEPA filter before exhausting sample gas
  - Data acquisition system

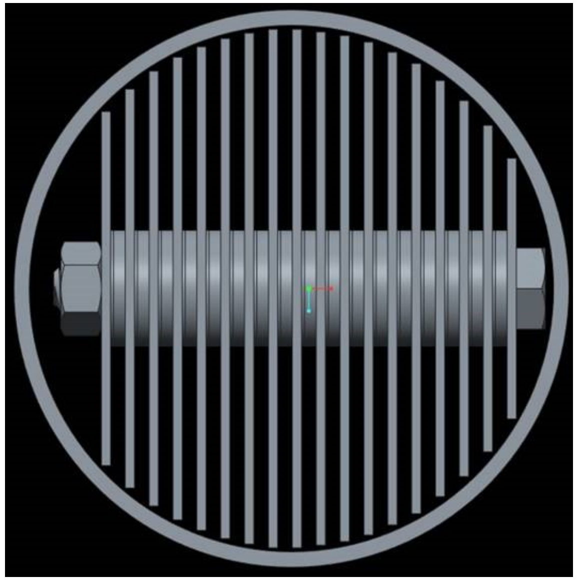


Instrumentation connected to 6-in. diameter test canister

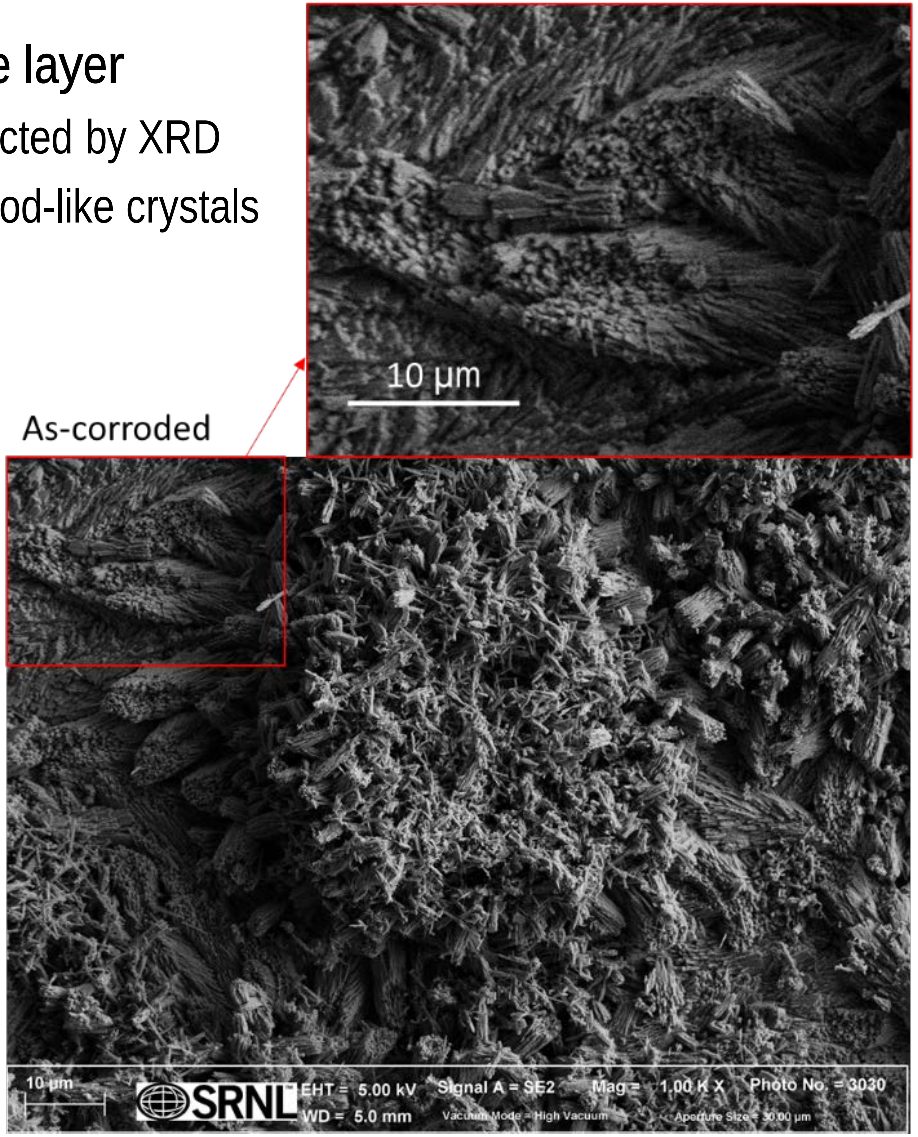
Samples

Surrogate coupon assemblies

- Parallel plates held together by bolt
- Spacers to maintain gap
- Maximizes sample area in mini-canister
- Corroded in-lab
  - Room-temperature water
  - 30+ days



- Oxyhydroxide layer
  - Bayerite detected by XRD
  - SEM shows rod-like crystals
  - ~9 µm thick



Mini-canister loading

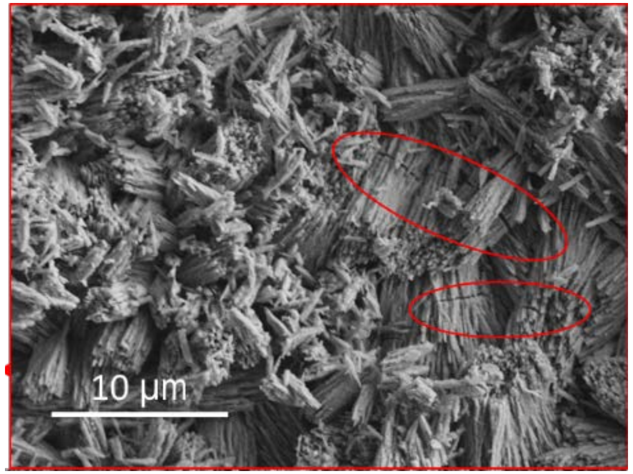
- Assembly loaded and sealed in canister
- Residual air elimination
  - Held under vacuum 12 h
  - Four He purges (alternating helium fill and vacuum)
- Helium backfill to 25 psia
- Two tests with identical assemblies
  - “As-corroded” (no further drying)
  - “As-dried” (additional heated drying step)

As-dried assembly

- Thermal drying
  - Sampling line left open on sealed canister
  - Canister heated to 220°C in air for 4 h
  - Vacuum for 1 h at 220°C
  - Residual air elimination and He backfilling procedure

- Impact of drying on oxyhydroxide
  - Reduced bayerite peaks and increased boehmite peaks in XRD
  - Caused minor cracking

Visible water release through sampling line during heating



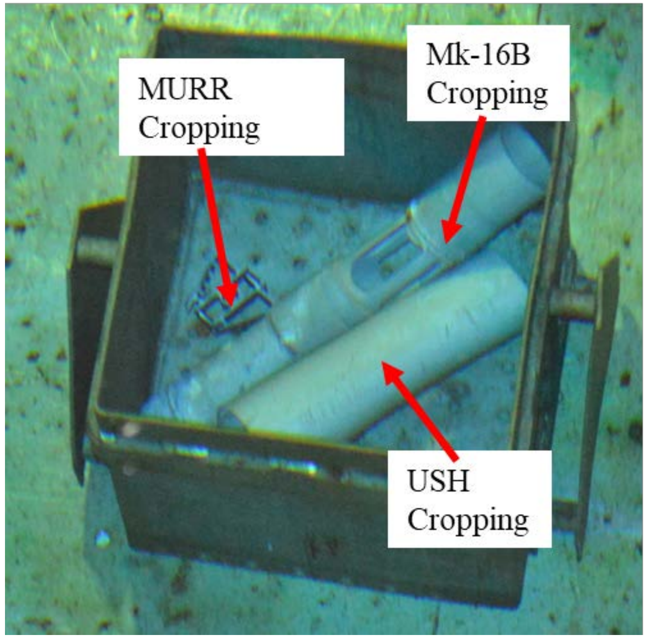
Small cracks in oxide after drying

Reactor-exposed samples: MURR fuel assembly cropping

- Retrieved from L-Basin wet storage at Savannah River Site
  - Aluminum pieces irradiated in-reactor
  - Do not contain fuel

SRS
L Basin

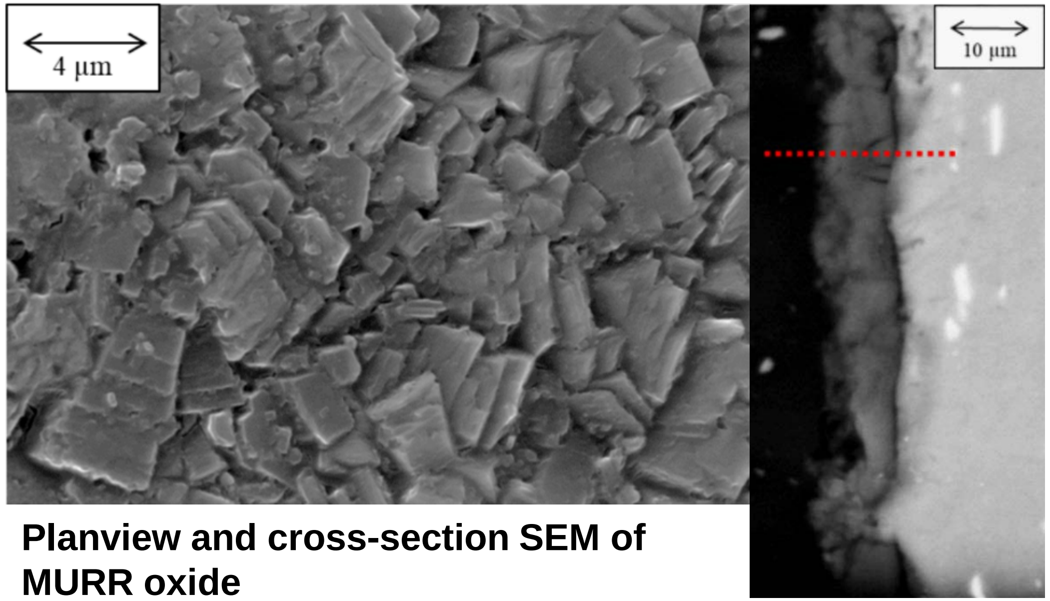
- From Missouri University Research Reactor (MURR)
- Al-6061
- Operating conditions: >60°C, 113 days
- Wet storage <18 years at ~30°C



Sampled materials collected in L-Basin

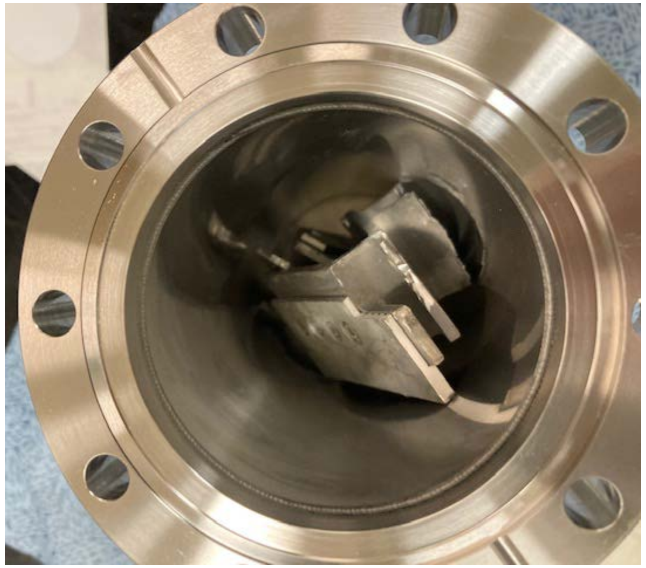
MURR in mini-canister

- MURR oxyhydroxide layer
  - Bayerite and boehmite detected by XRD
  - Relatively uniform blocky oxide
  - ~10 µm thick



Planview and cross-section SEM of MURR oxide

- No drying except drip-drying in air
  - Provides bounding H_2 rate for this sample
  - Helium purges to remove residual air
- Small sample compared to surrogates
  - Less H_2 generation expected
  - Larger gas volume → H_2 more diluted



MURR in mini-canister

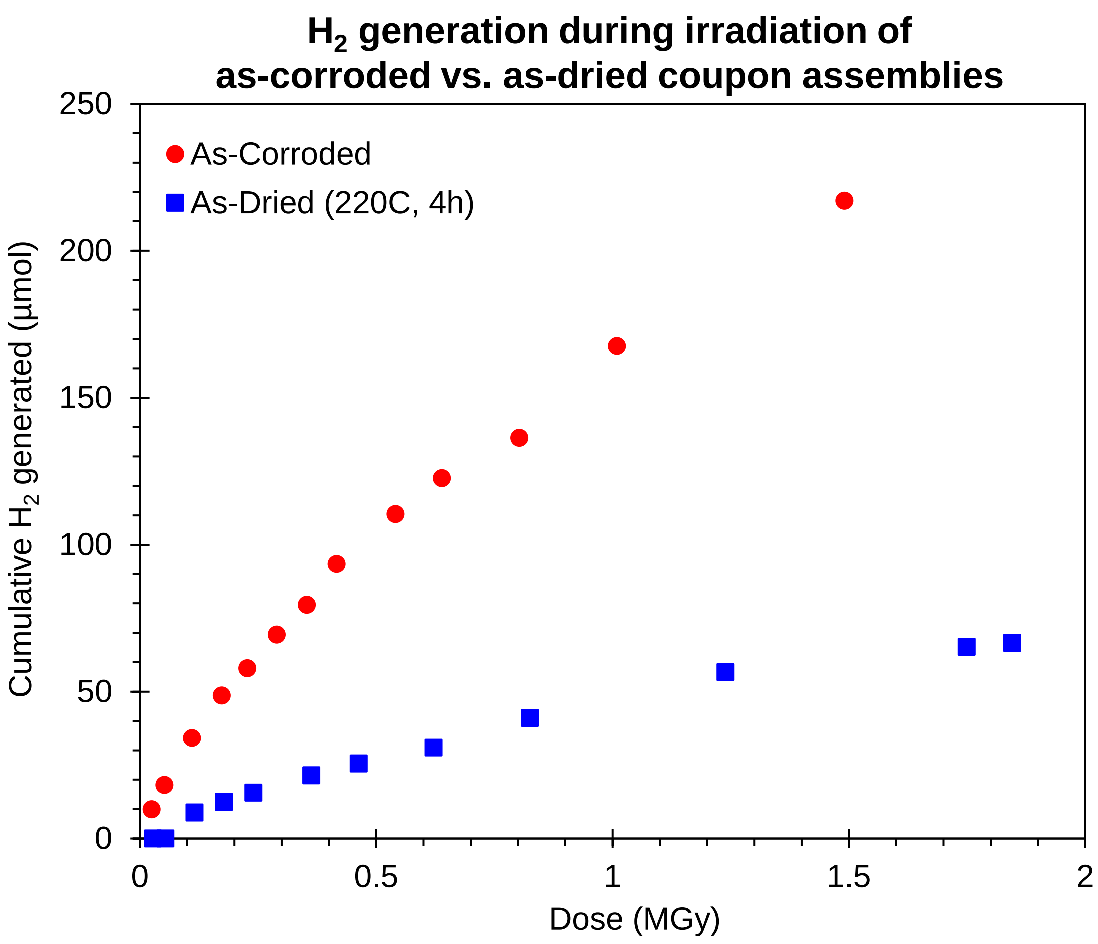
Results

Results: Surrogate coupon assemblies

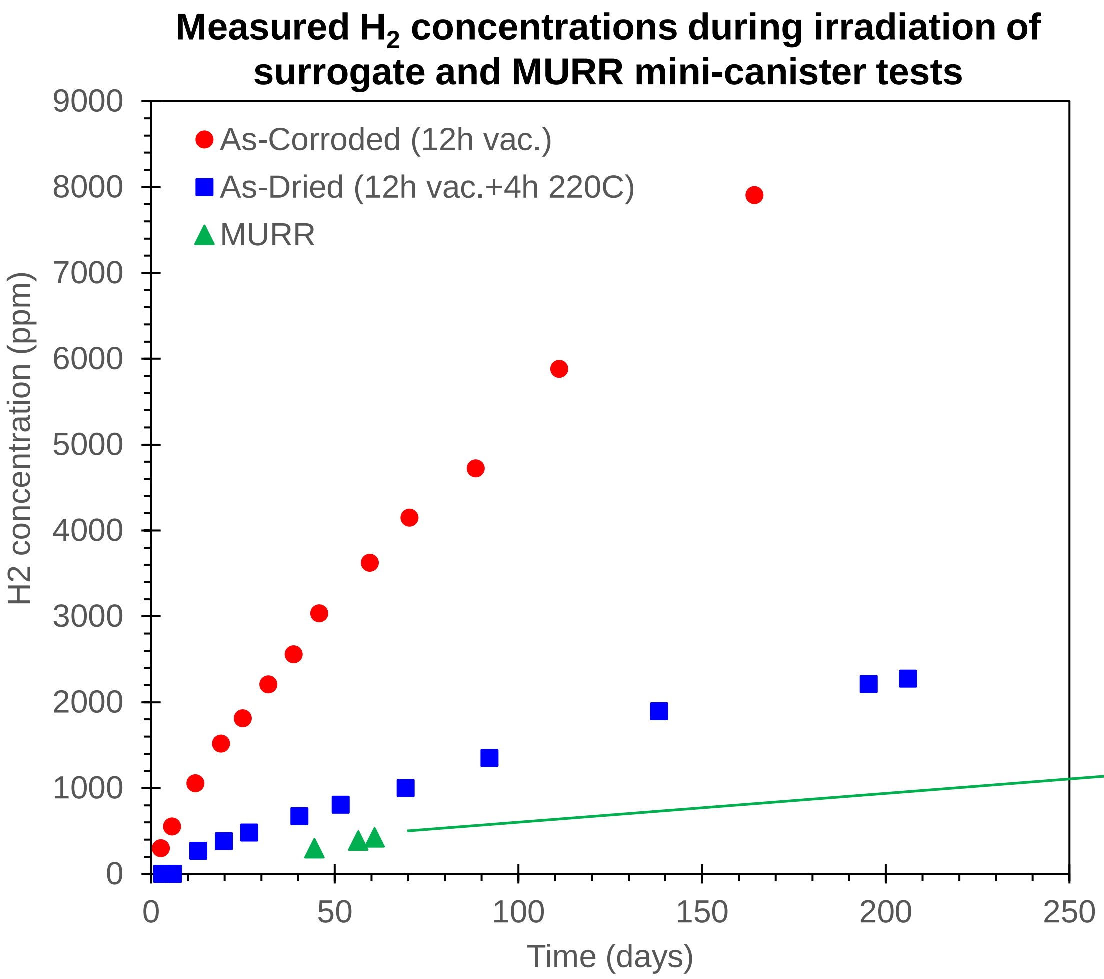
- H_2 generation rate much lower for as-dried than as-corroded surrogate

- Large difference in overall H_2 yield
  - As-dried assembly appears to be leveling off by ~2 MGy dose
  - As-corroded assembly yield ~3x larger at ~1.5 MGy and still climbing

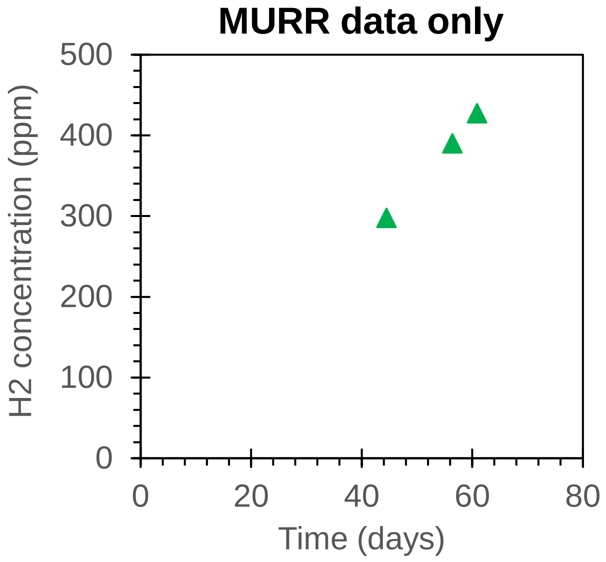
- Heated drying of ASNF canisters to 220°C has potential to greatly reduce H_2 generation



Results: Reactor-exposed material



- Small but increasing H_2 concentration observed
  - Smaller than for surrogate assemblies at same time/dose
  - Smaller sample requires longer to accumulate H_2
- Preliminary calculations suggest H_2 generation *per unit surface area* greater than as-corroded assembly
  - Consistent with lack of thermal *or* vacuum drying for MURR
  - Recent ampoule tests showed 12-h vacuum significantly reduced H_2 yield



Conclusions and path forward

- As-corroded and as-dried surrogate tests demonstrate that elevated-temperature drying can reduce radiolytic hydrogen generation
  - As-dried sample had
    - *Lower H_2 generation rate from beginning of test*
    - *Apparent plateau or transition to much lower generation rate at fraction of the H_2 yield of the as-corroded sample*
  - This data will be used in combination with drying experiment results to select drying parameters for dry storage applications
- Modeling
  - Data on the H_2 generation rates and plateau will be used to compare to model predictions
  - H_2 generation rates for the as-dried condition can be incorporated into the model to enable estimation of canister conditions following an appropriate drying condition.
- MURR test to continue to obtain H_2 yield curve for reactor-exposed material
  - Provides validation for H_2 generation rates obtained from surrogates

Reports: Instrumented Lid system

- *Task Technical and Quality Assurance Plan for Development of the Instrumented Lid for Dry Storage of Aluminum Spent Nuclear Fuel*, SRNL-RP-2019-00225, March 2019, D. Herman and J. McNamara.
- *Instrumented Lid – System Final Design*, SRNL-L2240-2019-00002, May 2019, J. McNamara and B. Randall.
- *Instrumented Lid Detailed Design*, SRNL-L2240-2019-00003, June 2019, J. McNamara and A. McNight.
- *Instrumented Lid – Assembly of System Components*, SRNL-L2240-2019-00024, August 2019, J. McNamara, D. Pak, A. McNight.
- *Instrumented Lid – System Functionality Testing*, SRNL-L2240-2019-00004, September 2019, J. McNamara and B. Randall.
- *Instrumented Lid – Fabrication of Basket*, SRNL-L2240-2019-00006, December 2019, J. McNamara, D. Pak, A. McNight.
- *Status Update on the Instrumented Lid Project*, SRNL-L2240-2019-00007, December 2019, J. McNamara, B. Randall, D. Pak, A. Duncan, A. McNight, H. Sessions, A. Baldwin, D. Hunter
- *Instrumented Lid – Full Instrumentation System Testing*, SRNL-L2240-2019-00005, Rev. 1, February 2020, J. McNamara, B. Randall, D. Pak, A. Duncan, A. McNight, H. Sessions, A. Baldwin, D. Hunter.

Reports: Mini-canister radiolysis experiments

- *Aluminum Spent Nuclear Fuel 2020 Large Sample Radiolysis and Measurement Test Plan*, SRNL-RP-2020-00219, April 2020, J. McNamara and C. Verst.
- *Instrumented Lid – Fabricate Hydrated Oxide Specimens for Testing*, SRNL-L6000-2020-00034, August 2020, J. McNamara and C. Verst.
- *Instrumented Lid – Initiation Irradiation and Measurement of As-is Hydrated Oxide Specimens (Large Coupons)*, SRNL-L6000-2020-00034, August 2020, J. McNamara and C. Verst.
- *Initiation Irradiation and Measurement of Dried Hydrated Oxide Specimens (Large Coupons)*, SRNL-L6000-2020-00046, September 2020, C. Verst, B. Randall, J. McNamara.
- *Interim Irradiation and Measurement of As-dried vs As-corroded Hydrated Oxide Specimens (Large Coupons)*, SRNL-L6000-2021-00006, March 2021, C. Verst, A. d'Entremont, B. Randall, J. McNamara.

Thank you!