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Technology Development for Aluminum-clad Spent Nuclear Fuel for Extended Dry Storage – Status Report

October 14, 2020

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LIST OF ABBREVIATIONS

3D	Three Dimensional
ASNF	Aluminum-Clad Spent Nuclear Fuel
ATR	Advanced Test Reactor
CFD	Computational Fluid Dynamics
CY	Calendar Year
DAQ	Data Acquisition
DOE	Department of Energy
DSC	DOE Standard Canister
EDS	Energy Dispersive Spectroscopy
EM	DOE Office of Environmental Management
EMTD	DOE-EM, Office of Technology Development
FGD	Forced Helium-Gas Dehydration
GC	Gas Chromatograph
HFIR	High Flux Isotope Reactor
IFSF	Interim Fuel Storage Facility
INL	Idaho National Laboratory
INTEC	Idaho Nuclear Technology and Engineering Center
IFSF	Irradiated Fuel Storage Facility
MURR	Missouri University Research Reactor
NE	Nuclear Energy
PFIB	Plasma Focused Ion Beam
PLC	Programmable Logic Controller
RH	Relative Humidity
RTR	Research Test Reactor
SEM	Scanning Electron Microscopy
SNF	Spent Nuclear Fuel
SNFWG	Spent Nuclear Fuel Working Group
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
TD	Technology Development
TEM	Transmission Electron Microscope
USH	Universal Sleeve Housing
V&V	Verification & Validation
XRD	X-ray Diffraction

1.0 Executive Summary

A task group under the Spent Nuclear Fuel Working Group of the U.S. Department of Energy (DOE), Offices of Environmental Management (EM) and Nuclear Energy (NE) identified technical challenges (“information gaps”) to the ability to provide for safe extended (>50 years) dry storage of Aluminum-Clad Spent Nuclear Fuel (ASNF) in a report issued in 2017 [1]. An Action Plan was developed [2], and a task-based program was launched under the sponsorship of DOE-EM, Office of Technology Development (EMTD) in October 2018 [3, 4] to close the gaps and complete the technical information set needed to implement extended dry storage with confidence.¹ This interim status report summarizes the work to date of this EMTD program to complete the technical bases and demonstrate that extended dry storage is safe and viable.

The overall technology readiness for deployment of a sealed canister, repository-road-ready system for ASNF is depicted by flowchart shown in Figure 1-1 below.

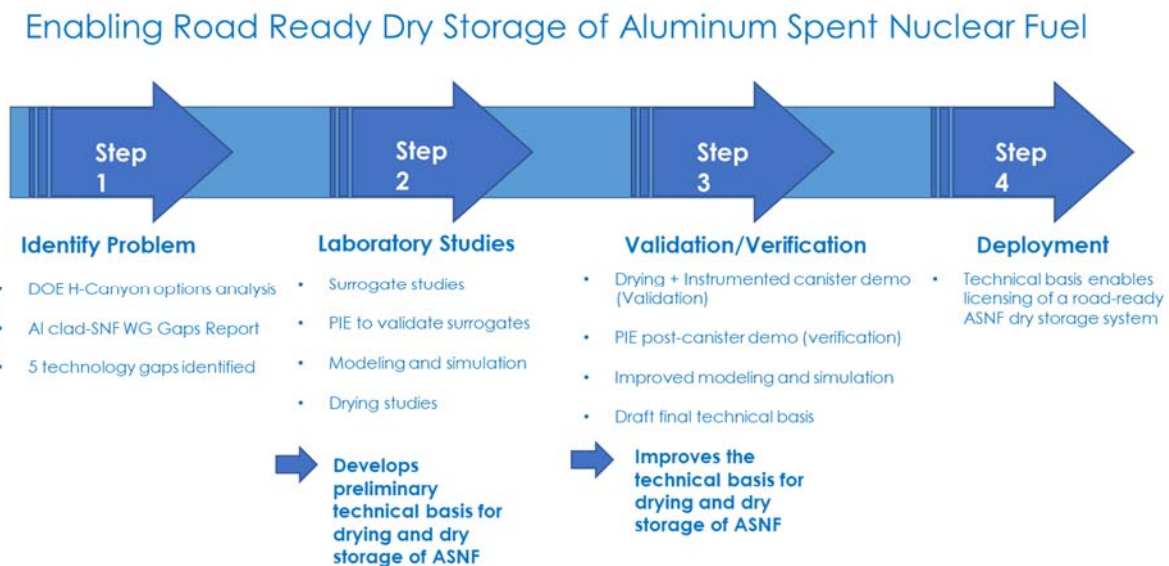


Figure 1-1. Flowchart to Establish and V&V the Technical Basis for ASNF-in-Canister Road-Ready Storage

The primary challenge to extended dry storage of ASNF is centered on the behavior of hydrated oxides, with radiolytic breakdown of adsorbed and chemically-bound waters associated therewith. Understanding of this behavior, and modeling of the performance of the ASNF-in-canister system, provides confidence to the engineered system that would be designed and deployed for drying and placement of the ASNF into canisters² for extended storage up to ultimate disposal. In the course of the planning and execution of the

¹ Dry storage of ASNF has been successfully implemented in the DOE complex at the Hanford site (aluminum-clad, uranium-core Single Pass Reactor fuel in the Multi-Canister Overpack canister) and the Idaho site (Advanced Test Reactor fuel) in the Irradiated Fuel Storage Facility (IFSF), building CPP-603, at the Idaho Nuclear Technology and Engineering Center. The establishment of the technical basis, with V&V of the drying and dry storage system for extended dry storage of ASNF i) at the INTEC; and ii) in the sealed DOE Standard Canister, is the goal of the EMTD program.

² A canister design for DOE-owned SNF for its long-term storage followed by transportation to and disposal in a federal repository is the “DOE Standard Canister.” The DOE Standard Canister was designed in the late 1990s and was intended to accommodate the full variety of DOE-owned spent nuclear fuel that would ultimately be transported to and co-disposed with DOE High Level Waste canisters in a waste package as part of the engineered barrier system in the federal repository. The initial canister design is contained in DOE, 1999, “Preliminary Design Specification for Department of Energy Standardized Spent Nuclear Fuel Canisters: Volume I - Design Specifications,” DOE/SNF/REP-011, Volume I and II, Revision 3, August 1999.

technology development work, it was determined that interpretation and application of the radiolytic gas yield results from the ASNF material system required additional clarification and data to better understand the results for application to the model for the prediction of the evolution of the gas composition and pressure of the ASNF-in-canister. The remaining and newly-scoped EMTD activities, as outlined in this report, were initiated in mid-FY20 are expected to be completed in FY21.

The EMTD-funded work on radiolytic behavior of the hydrated oxides and the modeling of the performance of ASNF-in-canister configurations completed to date has been subjected to an independent expert technical review by subject matter experts from the Pacific Northwest National Laboratory. The recommendations from those reviews (pending) may prompt additional testing/analyses that are expected to be conducted and completed in FY21. The completion of the in-progress activities, and any additional activities that would be prompted by the independent review, would complete the Step 2 activities. This will complete a comprehensive set of information and an analysis tool for the technical bases for long-term storage up to ultimate disposal of ASNF in a canister.

A significant portion of the activities to move ahead with Step 3, Validation/Verification, will also be nearing completion in FY21. These include a recommended drying protocol, a constructed and readied instrumentation system to monitor the proposed dry storage demonstration, and further refinement of the model for the performance of the ASNF-in-canister configuration over time as subject to stressors of temperature and attendant radiation.

To complete the Validation/Verification of Step 3, it is envisioned (planning and funding TBD) to perform a lead-surveillance canister demonstration project by loading and drying of Advanced Test Reactor (ATR) fuel in the DOE Standard Canister (DSC) and monitoring its in-canister performance. The demonstration, as envisioned, would be conducted at the Idaho National Laboratory (INL), Idaho Nuclear Technology and Engineering Center. Additional dry storage demonstrations may be recommended to address the recovery and drying of an inventory of ASNF that includes breached-cladding ASNF, an inventory of which (less than 7 % by number of assemblies) is in the L Basin at the Savannah River Site (SRS).

ASNF Dry Storage Technical Bases for Extended Dry Storage – Challenges Addressed by EMTD

The technical basis to enable safe, successful extended dry storage of ASNF, road-ready for repository disposal, is largely contained in documents listed in the bibliography to reference 1. The remaining technical information gaps are being addressed in the EMTD program [2] with several additional separate activities to revisit the structural capacity of the DSC [5]. All work completed to date to close the technology gaps support the technical basis to show that extended dry storage is safe and viable.

The EMTD-funded work provided corrosion and radiolytic behavior of ASNF and a detailed characterization of the condition of fuel material missing in the prior information base. This new information has been input into an analytic model developed to provide performance estimation of the ASNF-in-canister. The EMTD work was conducted through task-level activities. The activities were performed in collaboration by research staff at the INL and the Savannah River National Laboratory (SRNL). These activities have been largely completed as of the end of September 2020. This interim status report provides a summary of the work accomplished and the primary findings as well as a listing of the reports issued to date.

The distinguishing feature of ASNF is the hydrated oxides, also termed (oxy)hydroxides, that form on aluminum cladding of fuel by virtue of service exposure including the histories of reactor irradiation and post-discharge wet and/or dry storage. Key activities included the detailed characterization of the hydrated oxide films from: i) ATR fuel following a history of irradiation followed by wet and dry storage; and ii) from several fuels with irradiation and wet storage histories from L Basin at SRS.

Radiolytic gas generation (H_2) is a challenging phenomenon to dry storage that occurs with hydrated oxides under gamma radiation exposure. First-time data on radiolytic yield from hydrated oxides-on-aluminum substrates has been generated in the EMTD-funded activities. Radiolytic yield parameters were input into a three-dimensional multi-physics coupled thermal-chemical system model of ASNF-in-canister with configurations of fuel/canister loading into the DSC; initial cover gas; and hydrated oxide layer thickness so as to predict the response for any ASNF-in-canister storage configuration. Large amounts (e.g. ~ 60 vol.%) of H_2 with a corresponding total canister pressure of 5.5 atm were predicted to be produced in the DSC with a full load of ASNF with a bounding hydrated oxide layer thickness (34 μm for ATR ASNF) over a 50-year storage interval. However, extremely small levels of oxygen (O_2) are also predicted (10^{-8} vol. %); therefore, flammability concerns can be eliminated as a safety concern using oxygen-control credit in which the limit for oxygen is 5% volume.

Considering impacts on pressure, the maximum H_2 molecular concentration from a hydrated oxide layer (e.g., boehmite or $Al_2O_3 \cdot H_2O$) that could theoretically be released is the same molecular concentration as the water (H_2O) itself. With the full (but non-realistic) breakdown of the H_2O , there would be a molecular concentration of gas 1.5 times that of H_2O from H_2 and $\frac{1}{2} O_2$. The effect of the bound water on canister pressurization for ASNF in a DSC has been analyzed previously in reference 9. The maximum pressure was determined to be 22.7 atm at 315°C.

The maximum amount of bound water after a drying treatment will be evaluated following the completion of the drying testing in FY21. Even without removal of any of the chemically-bound water, it is fully expected that canister pressurization (a function of free volume, amount of water {residual free and chemically-bound water}, and temperature) will be well within the structural capacity of the DSC [5] with a load of ASNF. It is important that any reduction in the free volume, for example by filling with a neutron absorber, be considered in the canister pressure evaluation.

Therefore, a preliminary major conclusion from the EMTD-funded work is that thermal decomposition of bound water and/or radiolytic gas generation results in a non-flammable and a non-corrosive gas environment at pressures that do not challenge the structural integrity of the canister design and storage facility for safe extended storage. Nevertheless, the accurate prediction of the performance of ASNF-in-canister, with time, is important to provide confidence to the Department to embark on this disposition pathway.

A three-dimensional multi-physics computational fluid dynamics model of the ASNF canisters has been developed. The model can be applied to both sealed and vented canister configurations. The model has demonstrated the ability to show transient conditions over long simulation time periods for extended storage applications, for cases with any combination of loaded ASNF conditions including oxide thickness, heat source, residual free water, and cover gas. An important input to the model is the rate of radiolytic hydrogen generation that controls the rise in hydrogen with time.

Several additional activities were initiated in FY20 and will be completed in FY21. These include: 1) the scale-up drying test campaign to investigate drying approaches for a charge of mock full-scale MTR-design³ assemblies with oxides in a one-basket level, 1/3-size DSC (Task 5 activity); 2) additional radiolysis testing to evaluate: i) high-dose (post-linear trend) conditions; ii) effect of helium cover gas on hydrogen yield; and iii) testing of actual spent nuclear fuel (SNF) cladding using L Basin specimens with mixed hydrated oxides, before/after a drying treatment to evaluate radiolytic gas yield in comparison to previous cold surrogates (Task 2 activity); and 3) radiolysis testing of a scale-up size of simulated ASNF fuel plate with a hydrated-oxide layer, before/after drying treatments for long-term monitoring using the instrumented lid

³ The mock full-scale or surrogate assemblies are of a generic Materials Testing Reactor (MTR) plate fuel design

sensor system (Task 2, Task 3, and Instrumented Lid activity). The scale-up plate testing will include the coupled-chemical system modeling of the mini-canister system as developed in Task 3 of the EMTD-funded work.

The overall preliminary conclusions from this technology development program including the anticipated successful completion of the FY21 activities are:

- 1) The testing and analysis results of the characterization of ATR fuel, and the performance modeling in its storage configuration, show that the ASNF presently in vented interim dry storage (IFSF) is safe for continued, extended dry storage (> 50 years) without corrosion degradation challenges;
- 2) The testing and analysis results of ASNF from L Basin can be safely placed in sealed canister storage without corrosion degradation, canister pressurization, and canister flammability challenges pending ultimate disposition;
- 3) The ASNF-in-canister performance modeling, including the H₂ generate rate inputs from extensive radiolysis testing of hydrated oxides on aluminum substrate testing allows reliable performance prediction of configurations of ASNF-in-canisters including parameters of temperature, gas space evolution, and canister pressurization.

The integrated EMTD-funded tasks will have closed the identified knowledge gaps regarding hydrogen generation and oxide performance of ASNF during extended dry storage. The integrated tasks are described below in the Introduction section of this status report (see Figure 2-1). That is, the technical bases for enabling extended vented dry storage and sealed dry storage for ASNF have been fully established.

The next step being planned for dry storage technology readiness is a hot demonstration to provide verification of the ASNF behavior results, and validation that the ASNF-in-DSC can be safely deployed for road-ready disposition for ASNF. For this purpose, a special-design instrumented lid to be attached to a DSC has been designed and constructed. The work to develop the instrumented lid for a prospective demonstration project at INL is summarized in this report.

The work in this report contains results and information prepared under INL Quality Assurance Plan [6] and SRNL Task Technical and Quality Assurance Plan SRNL-RP-2018-00610 [7].

2.0 Introduction

A task group under the Spent Nuclear Fuel Working Group (SNFWG) of the U.S. Department of Energy (DOE), Offices of Environmental Management (EM) and Nuclear Energy (NE) identified challenges to the long-term (>50 years) storage of aluminum-clad spent nuclear fuel (ASNF) [1]. An Action Plan was developed, and a technology development program under the sponsorship of DOE-EM was launched [2-4].

This status report provides a status of the work in technology development for ASNF long-term dry storage, and it outlines the major project elements needed in the design and deployment of a road-ready dry storage system for ASNF. The DOE SNFWG's report on technical considerations and challenges for extended dry storage of ASNF entitled, *Aluminum-Clad Spent Nuclear Fuel: Technical Consideration and Challenges for Extended (>50 Years) Dry Storage*, DOE/ID RPT-1575, June 2017 [1] identified five knowledge/technical data gaps that need to be addressed to help inform decision-makers on the environmental, safety, and long-term programmatic risks associated with a management strategy for ASNF in extended (i.e., greater than 50 years) dry storage. These knowledge gaps and technical data needs are:

- A- Behavior/chemistry of oxyhydroxide layers for the range of ASNF fuel designs and dry storage configurations,
- B- Resolution of radiolytic gas generation data for ASNF oxyhydroxide layers,
- C- Combined effect of episodic breathing and radiolytic generation of potentially corrosive gases in sealed and vented systems,
- D- Performance of research test reactor (RTR) ASNF in existing dry storage systems,
- E- Effects of high-temperature (i.e., greater than 100°C) drying on the chemistry and behavior of oxyhydroxide layers.

The DOE SNFWG report also made several recommendations including one to develop an action plan to identify needed technical and engineering activities and analyses to address the identified knowledge gaps and technical data needs. A team composed of twenty spent nuclear fuel management experts and appropriate subject matter experts from the Idaho National Laboratory (INL) and Savannah River National Laboratory (SRNL) was assembled. Leads from each institution were identified for each of the five need areas and charged with developing a problem statement, research questions, proposed research scope, identification of interface needs with other identified need areas and expected research outcomes.

An action plan was developed to generate appropriate data to address the knowledge gaps. The action plan is documented in “*Aluminum Clad Spent Nuclear Fuel Long Term Dry Storage Technical Issues Action Plan – Technical and Engineering Activities*”, INL/EXT-17-43908 [2]. This report describes the technical, engineering and modeling activities and analyses that address previously identified knowledge gaps and technical data needs presented in the DOE SNFWG's report [1]. The plan included six focused tasks as listed in Table 1.

Table 1. Listing of the Six Specific Program Tasks to Address the Knowledge Gaps

Task 1: Oxyhydroxide Layer Behavior and Chemistry; Evaluations included studies of ASNF cladding oxide performances, extended storage impacts, and hydrogen generation from corrosion mechanisms.
Task 2: Oxide Layer Radiolytic Gas Generation: Information generated focused on the gamma radiation-induced hydrogen generation from pre-corroded aluminum alloy 1100 coupons.
Task 3: Sealed and Vented System Episodic Breathing and Gas Generation Prediction: This task is focused on an integrated model of the sealed and vented storage container systems, using three-dimensional multi-physics computational fluid dynamics (CFD) models and simulations for prediction of oxide performance, container environment, and gas generation during storage.
Task 4: Performance of ASNF in Dry Storage: In support of the modeling and storage performance predictions, this task provides a characterization of the ASNF from the Advanced Test Reactor (ATR) that have a dry storage service history.
Task 5: Oxide Layer Response to Drying: This task involves modeling of canister drying via (a) forced helium and (b) vacuum drying. Included in the test plan is a set of engineering-scale drying tests to verify the modeling and to generate empirical parameters.
Task 6: Surrogate Sample Preparation and Validation Experiment: Experiments were performed to produce hydroxide (oxide) films on aluminum alloys (1100, 5052 and 6061) used for fuel cladding. The characteristic oxide morphologies, thicknesses and chemical compositions were determined for use in modeling and ASNF performance in canisters during long term storage. This task includes the characterization of selected specimens of ASNF from the SRS L Basin.

These six tasks were developed to provide the information to fill the identified knowledge gaps and to provide needed data. Table 2 shows the relationship between the knowledge gaps and the corresponding tasks that provide data and information to answer cover each gap.

Table 2. Relationship of Specific Tasks (1 through 6) to Address Knowledge Gaps and Data Needs (A through E)

Knowledge Gaps and Data Needs	Task 1	Task 2	Task 3	Task 4	Task 5	Task 6
A. Behavior/chemistry of oxyhydroxide layers for the range of ASNF fuel designs and dry storage configurations	X			X		X
B. Resolution of radiolytic gas generation data for ASNF oxyhydroxide layers		X	X			
C. Combined effect of episodic breathing and radiolytic generation of potentially corrosive gases in sealed and vented systems	X	X	X	X		X
D. Performance of RTR ASNF in existing dry storage systems			X	X		
E. Effects of high-temperature (i.e., greater than 100°C) drying on the chemistry and behavior of oxyhydroxide layers.	X	X			X	

The six tasks have a common focus to provide a tool to assess the performance of ASNF in a long-term (50+ years) storage container environment. The modeling developed in Task 3 along with the empirical data and modeling produced in other tasks combine to produce the performance predicting tool as schematically depicted in Figure 2-1.

The investigation on drying technologies to enable dehydration of hydrated oxides (Task 5) is still in progress and is expected to be completed in early FY21. This present report includes a status of testing performed to date.

The design and fabrication of an instrumented lid for the dry storage canister was added to the technology development (TD) program to ready for the next phase of technology completion. The lid provides real time data regarding the canister environment during initial testing and longer-term storage test, verifying that the fuel temperature and gas space compositions (e.g., hydrogen and oxygen levels) are well-within estimated from the analytical model. The lid fabrication is scheduled to be completed in 2020. At the completion of the drying technology selection work, and the lid fabrication, it is planned, currently unfunded, that a scaled demonstration with ASNF will be initiated at INL with ATR fuel as part of full-scale dry storage technology readiness demonstration.

The following is the status of the tasks in the TD program including the citation of the reports issued to date for each task. The previous information base that this new information supplements is provided in “selected bibliography on ASNF” contained in reference 1.

The completion of the TD activities in FY21 would enable an engineering design of a system for drying and extended dry storage of ASNF with defensible technical basis.

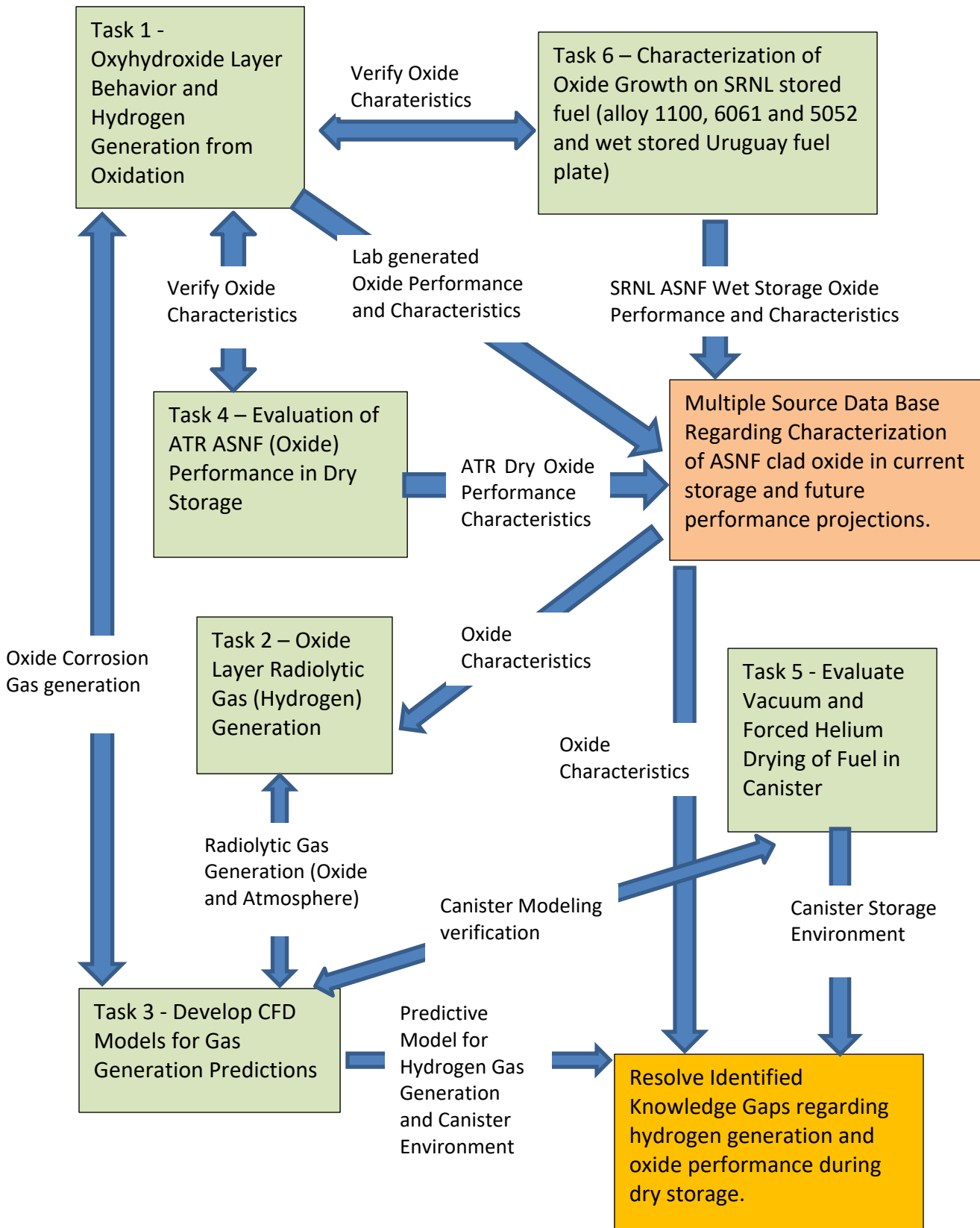


Figure 2-1. Schematic Showing Paths of Program Information Integration

3.0 Task Summary

A summary description of the investigations and the results of each of the six tasks is described in this section.

3.1 Task 1 – Hydrated Oxide Layer Growth Behavior. Task lead Tedd Lister, INL

The following reports have been issued from Task 1 of this program:

Aluminum Clad Spent Nuclear Fuel Task 1: Oxyhydroxide Layer Behavior and Chemistry Experimental Test Plan, INL/EXT-18-45857, July 2018, T. Lister.

Modeling Activities Concerning Aluminum Spent Nuclear Fuel Cladding Integrity, INL/EXT-18-51694, December 2018, M. Glazoff and T. Lister.

Vapor Phase Corrosion Testing of Pretreated AA1100, INL/EXT-18-52249, December 2018, T. Lister.

Analysis of Vapor Phase Corrosion of Pretreated Aluminum Alloys, INL/EXT-19-55558, August 2019, T. Lister and C. Orme.

Vapor Phase Corrosion Testing of Pretreated AA6061 and AA5052, INL/EXT-19-53964, May 2019, T. Lister and C. Orme.

Vapor Phase Corrosion of Pretreated Aluminum Alloys: Final Report, INL/EXT-19-56497, Revision 0, November 2019, T. Lister and C. Orme.

Corrosion testing to evaluate vapor phase corrosion (water vapor-aluminum reactions) of the set of aluminum cladding alloys (AA1100, AA6061, and AA5052) was investigated in this task. The testing included pretreatment or prefilming of two types: Type 1 prefilm specimens were prepared to produce boehmite (AlOOH) of an average thickness between 1 to 2 μm for the alloys, with local variations observed; Type 2 prefilm specimens were of trihydrated oxide ($\text{Al}(\text{OH})_3$) and had film thicknesses of between 5.6 to 5.7 μm for the alloys. Sensitive gravimetric measurement and cross-section microscopy were used to determine the prefilming oxide thicknesses.

Special testing apparatus to control and measure relative humidity (RH) (25, 75, and 100%) and temperature (20, 50, 100, and 180°C) exposure at high sensitivity was designed and built, and tests in the apparatus were conducted for 3-week exposures. Sensitive gravimetric measurements were used to evaluate the changes to the hydrated oxides.

The results showed no weight gain for any of the test conditions, within measurement uncertainty; to the contrary, significant weight loss was observed for most of the specimens, including Type 1 and 2, particularly at the 180°C test condition. This is attributed to thermal dehydration (loss of chemisorbed water) of the oxides.

The overall conclusion is that no hydrogen is expected to be produced due to corrosion of the hydrated oxide layers in a range of temperatures and including (inadvertent) free water creating a humidity condition expected for ASNf in a dry storage canister. This is attributed to the protection or passivating feature of the oxides against further vapor corrosion.

3.2 Task 2 – Radiolytic Gas Generation. Task leads Greg Horne, Peter Zalupski, and Elizabeth Parker-Quaife, INL; and Chris Verst, SRNL.

The following reports have been issued under Task 2 of this TD program:

Aluminum Clad Spent Nuclear Fuel Task 2: Oxide Layer Radiolytic Gas Generation Resolution Experiment Test Plan, INL/EXT-18-45858, July 2018, P. Zalupski.

Radiation-Induced Changes in Corrosion of AA1100, INL/EXT-19-52738, Rev. 1., February 2019, E. Parker-Quaife, G. Horne, C. Heathman, P. Zalupski.

Radiation-Induced Molecular Hydrogen Gas Generation by Pre-Corroded Aluminum Alloy 1100, INL/EXT-19-55202, Rev. 2, September 2019, E. Parker-Quaife, G. Horne, C. Heathman, C. Verst, P. Zalupski.

Radiation-Induced Molecular Hydrogen Gas Generation by Pre-Corroded Aluminum Alloy 1100 – FY20 December Update, December 2019, E. Parker-Quaife, G. Horne, C. Heathman, and P. Zalupski.

Evaluation of Radiolysis Data of Hydrogen Gas Generation During Gamma Irradiation of Oxidized and Non-Oxidized Aluminum Samples, SRNL-STI-2020-00147, Rev. 0, April 2020, R. Kesterson, R. Sindelar, C. Verst, G. Horne, E. Parker-Quaife.

Aluminum Spent Nuclear Fuel 2020 Radiolysis Test Plan, SRNL-RP-2020-00187, Rev. 1, June 2020, C. Verst.

Oxide Layer Radiolytic Gas Generation Resolution: Task 2 Experimental Design, C. Verst, C. Crawford, E. Parker-Quaife, G. Horne, P. Zalupski.

This task developed radiolytic yield data for multiple sets of samples of hydrated oxides irradiated with ^{60}Co gamma sources at INL, Notre Dame, and SRNL laboratories, and with subsequent measurement of hydrogen released.

The evaluation of H_2 generation in a chemical system under ionizing radiation can be broken into two regimes:

- Initial radiolytic product generation rate regime, which is where a linear yield with dose, from which G-values (# of molecules of radiolytic species or products per 100 eV of energy deposited into the material) are evaluated,
- “Steady-state” chemistry condition which is the chemical equilibrium at a defined radiation exposure rate and temperature for a closed chemical system. This regime is not readily determined as slow material interaction reactions (e.g., H_2 uptake into a metal substrate) could occur to impact the evolution of the gas space chemistry.

The set of radiolytic gas generation results from the testing to date are compiled in Table 3. The radiation test conditions included various cover gases and relative humidity conditions. A mixed oxide (bayerite-boehmite) film on Al6061 was used as the test system. Two methods for evaluation of hydrogen generation from this oxide-on-substrate system can be used: The first method is to assume the radiolytic yield is based on gamma energy deposited into just the oxide (G_{oxide}). The second method is to assume the radiolytic yield is based on gamma energy deposited into both the oxide and substrate (G_{bulk}). Furthermore, the value for G_{oxide} can be further distinguished based on hydrated oxide type. The G values in Table 3 below were calculated using an estimate of the gamma absorbed specifically by the surface oxide mass. The absorbed

gamma dose in Table 3 below is the gamma energy deposited into the total sample mass (oxide and aluminum substrate).

The modeling work under Task 3 has used inputs for radiolytic hydrogen generation based on the Table 3 data. The additional testing in CY20 would likely result in data showing a lower rate of H₂ generation.

Table 3. G-values from Radiolysis Testing using ⁶⁰Co Irradiation of a Mixed Bayerite-Boehmite Film

gas phase	Relative humidity (%)	Absorbed gamma dose (kGy)	H ₂ production (μL)	G-values for boehmite (molecule/100 eV)	G-values for bayerite (molecule/100 eV)
Ar (max)	49	543	8.8	1.9313	1.8831
Ar (min)	0	1070	10.2	1.1441	1.1155
N ₂ (max)	52	978	7.0	0.8201	0.7996
N ₂ (min)	0	495	1.1	0.2639	0.2574
Ar (max)	0 (100 °C)	500	7.6	1.7449	1.7013
Ar (min)	0 (200 °C)	1000	11.3	1.3554	1.3215

Note: Two methods for evaluation of radiolytic hydrogen production from a hydrated oxide-on-aluminum substrate can be used. The first method is to assume the radiolytic yield is based on gamma energy deposited into just the oxide (G_{oxide}). The second method is to assume the radiolytic yield is based on gamma energy deposited into both the oxide and substrate (G_{bulk}). **The absorbed dose into the both the oxide and the substrate (bulk G) is the method recommended by the radiolysis task team to evaluate radiolytic hydrogen generation.** The G-values in the table consider the gamma energy deposited in the oxide only (G_{oxide}).

An evaluation of the radiolysis testing data collected to date including the notional phenomenological description of H₂ generation in a sealed canister system is contained in a separate topical report. [8]

3.3 Task 3 – Coupled Thermal/Chemical Modeling. Task Lead: A. Abboud, INL

The following reports have been issued under Task 3 of this TD program:

Aluminum Clad Spent Nuclear Fuel Task 3: Sealed and Vented Systems Episodic Breathing and Gas Generation Modeling Plan, INL/EXT-18-45860, July 2018, H. Huang and A. Abboud.

Transient Coupled Chemical-Thermal-Fluid Field Simulation for Sealed Aluminum-clad Spent Nuclear Fuel Storage Canister, INL/EXT-18-51683, Rev. 0, June 2018, A. Abboud and H. Huang.

Development of Transient Coupled Chemical-Thermal-Fluid Multiphysics Simulation for Unsealed, Vented Aluminum-clad Spent Nuclear Fuel Storage Canister, INL/EXT-18-51681, Rev. 0, September 2018, A. Abboud and H. Huang.

Sensitivity Study of Coupled Chemical-CFD Simulations for Sealed and Unsealed Aluminum-clad Spent Nuclear Fuel Storage Canisters, INL/EXT-19-52650, January 2019, A. Abboud and H. Huang.

Full-scale Model of Dry Storage of Aluminum Clad Spent Nuclear Fuel, INL/EXT-19-55185, July 2019, A. Abboud and H. Huang.

Guide to CFD-Chemical Model for Spent Fuel Storage, INL/EXT-20-58578, June 2020, A. Abboud.

Modeling of SRS Aluminum-Clad Spent Nuclear Fuel in Standard DOE Sealed Canisters, INL-EXT-20-57893, March 2020, A. Abboud.

As the first step toward developing three-dimensional (3D) multi-physics computational fluid dynamics (CFD) model for unsealed and vented canister storage system, a 3D CFD model coupled with bulk gas radiolysis reactions was developed first for sealed DSCs filled with inert gas and trace amount of air and water. The workflow for constructing canister-scale 3D CFD models and coupling with gas phase radiolysis reactions were established, which can be readily extended to unsealed, vented canister storage system. The milestone report documents the theory of the model, workflow to establish radiolysis reaction network, and initial simulations of the evolutions of thermal fields and hydrogen gas concentrations within sealed DSCs over long period of time.

As an initial step in the modeling of the dry storage Irradiated Fuel Storage Facility (IFSF), a model was constructed that incorporates upper bound results of radiolytic gas generation with flow patterns within the IFSF facility. The facility model incorporates rates of nitric acid generation from canister scale modeling to assess buildup in the facility. This is done for two scenarios, one with 400 canisters loaded, and one with the rack fully loaded with canisters and at the maximum heat load capacity rated for the storage facility. Even with conservative assumptions, the model shows no potential for accumulation of nitric acid within the facility under either scenario. In addition, the prior models for sealed and unsealed canister were updated to include surface chemistry of the boehmite decomposition reactions determined through experiments associated with other tasks of the project. The model now incorporates the decomposition of boehmite through radiolytic effects, dehydration of the pseudo-boehmite, and general corrosion of aluminum. No pitting or localized corrosion is considered. This assumption is justified as pitting and localized corrosion would be negligible to hydrogen generation.

For sealed canisters the model shows that under any case studied the hydrogen concentration reaches well above the 4% flammability limit, and can reach 2-5 atmospheres of total pressure due to the vast quantity of potential aluminum hydroxide that can be present, though the hydrogen production decreases over time as the model accounts for decreasing dose rate. However, there is no mechanism that releases significant amount of oxygen, and it exists in only trace (<ppt) amounts. If canisters are improperly sealed with a small amount of air present (1% by volume), there is the potential for on the order of 1000 ppm of nitric acid vapor to form. The fuel element decay heat and the aluminum hydroxide layer thickness present are the two most important parameters in determining the 50-year fuel history. Also note that the pressures generated are significantly below the pressure rating of the DSC.

In the unsealed canisters present in the IFSF, the model shows peaks of the minor species the initial few hours as steady-state is established, though the amount of hydrogen and nitric acid present decays after this initial period to negligible amounts of hydrogen and 10s of ppm of nitric acid as aluminum hydroxide is consumed and as the fuel dose rate decreases over time. Even during this peak generation, hydrogen concentration does not reach levels over the 4% flammability limit in any unsealed storage scenarios modeled. An example of a summary set of conditions for a sealed container is shown in Table 4. The values from the report utilize partitioned G-values from Table 3. No change to the trend of the results would be expected when it is changed to total sample weight – except that the thickness of the oxide layer would have only minor impact over the first 50 years. Overall a reduction of the pressure and hydrogen content would be seen across the cases.

Table 4. Summary of Conditions for a Sealed Container Model following 50-years Storage

	Sealed			Sealed + 1% air			
Case / Variable Max	Pressure (atm)	H ₂ (%)	O ₂ (%)	Pressure (atm)	H ₂ (%)	O ₂ (%)	HNO ₃ (ppm)
Base (18W, 10um thickness, 1% H ₂ O(g))	2.93	37.3	3e-9	2.93	37.7	0.21	745
Low decay heat (6W)	2.51	20.4	1e-9	2.50	20.6	0.21	308
High decay heat (42W)	3.34	45.2	8e-9	3.34	45.4	0.21	1380
Low H ₂ O% (.1%)	2.94	37.2	3e-9	2.94	37.6	0.21	743
High H ₂ O% (10%)	2.86	38.3	4e-9	2.86	38.7	0.21	765
Thin oxide (5 um)	2.24	23.5	2e-9	2.24	23.9	0.21	944
Thick oxide (15 um)	3.52	47.0	4e-9	3.52	47.4	0.21	626
Raised Exterior Temperature (+50 C)	3.58	36.4	3e-8	3.85	36.8	0.21	612
Loaded to 2000 W	3.69	46.6	2e-8	3.69	46.9	0.21	1901

Note: These results are based on application of G_{oxide} of 1.59 molecules of H₂/100 eV deposited into the oxide. If a bulk G value were used instead, the rate of hydrogen generation is reduced based on an alternate method to evaluate the results of Task 2 testing, and the total hydrogen in the canister at the 50-year time is lower than the results in

Table 4

Decay heat and oxide thickness have the largest effects of the generation of hydrogen and nitric acid within the canisters, whether sealed or unsealed. The decay heat of a loaded canister can be well controlled, as the decay heat for individual ATR fuel elements are well characterized. However, the hydroxide film thickness can vary greatly across the fuel elements and is difficult to measure on radioactive elements. While the recent work places the range for this layer on aluminum clad fuel in the ATR at 5-15 μm , based on Missouri University Research Reactor (MURR) samples and reduced enrichment tests some elements can contain up to 34 μm thickness (34 μm being the basis for DOE-SNF-REP-104 [9]), with a 22 μm average. It is unlikely that a fully loaded canister would contain all of fuel elements with the absolute maximum measured hydroxide thickness.

The current summary from this task is:

- A 3D coupled CFD model with chemical radiolysis of aluminum-clad spent nuclear fuel was developed for both sealed and unsealed canisters containing ATR fuel elements. The chemical model has been expanded from prior work to include hydrogen generation from radiolytic decomposition of aluminum hydroxide films, and general corrosion of aluminum hydroxide films and of pure aluminum. At the facility scale, no potential buildup of nitric acid vapor in the facility with vented storage is seen.
- Even in the worst-case scenario for the storage of ATR fuel in sealed canisters, the pressure of the canister only goes to 3.7 atm at high decay heat or 5.5 atm at extremely high hydroxide thickness, a significant decrease from 11.3-22.7 atm (at 315°C) estimated in DOE/SNF/REP-104.[9] The maximum is reached as a combination of consumed aluminum hydroxide layers, with a decreasing dose rate over time.

- c) While hydrogen is present well above the flammability limit, the chemical modeling shows that oxygen content is negligible.⁴ In addition, this simulated value for the pressure is a rather conservative estimate as it would require all fuel elements to be two standard deviations above the average fuel element in wet storage, and the radiolytic chemistry is solved with spatially constant dose rates, so it is likely the actual build-up of hydrogen and pressure in the canister would be less.
- d) Modeling of the sealed DOE canisters for MURR and High Flux Isotope Reactor (HFIR) fuel element showed that peak temperatures are not as high as the ATR packed canisters. In addition, the surface area to volume ratio is lower, these two results should bound the DOE sealed canisters with the ATR packaged modeling. Further validation of this is planned with the instrumented lid design described later. It may be possible that the small amounts of nitric acid predicted may need to be studied for additional corrosion impact, but only if residual air is present. Though the concentrations are likely small enough that no impact is seen.

The details of the modeling are documented in the listed reports, some specific items need to be noted regarding future comparisons with other data;

1. This primary modeling was based on ATR fuel storage and associated container design with its bounding: i) hydrated oxide (e.g. 34 μm) film thickness; ii) surface-to-volume ratio in the DSC; and iii) decay heat, vis-à-vis the expected ASNF inventory in the complex. Bounding ASNF from L Basin (MURR SNF) was also modeled to demonstrate the bounding fuel and model analysis results from the ATR fuel
2. For one example of the ATR fuel it was determined that the pressure release for the 50-year stored fuel approached 4 atmospheres of hydrogen as a quasi-worse case condition as shown in Figure 3-1:

⁴ The strategy for flammability control for ASNF-in-canister is to credit an oxygen limit. Previous work for the Multi-Canister Overpack for the DOE SNF at the Hanford site developed the engineering demonstration that an oxygen limit of 4 volume % is a non-flammable gas [CHPRC-01049, Rev. 0, MCO Internal Gas Composition and Pressure During Interim Storage at the Canister Storage Building, K. R. Bader, CH2MHILL, October 2010]. The US NRC also recognizes oxygen limit as a method for flammability control and suggest a 5 volume % limit with no associated temperature criterion [Inspection Enforcement Information Notice No. 84-72, Clarification of Conditions for Waste Shipments Subject to Hydrogen Gas Generation, US NRC].

Thus, flammability control can be met by limiting oxygen to less than 5 mole percent:

$$\frac{n_{\text{oxygen}}}{n_{\text{oxygen}} + n_{\text{hydrogen}} + n_{\text{helium}}} = 0.05$$

where n denotes the moles of oxygen, hydrogen, and helium in a canister. Stated in other words, flammability is only achievable if there is a sufficient amount of both hydrogen and oxygen in a gas composition. Flammability can be mitigated by ensuring a low oxygen volume (mole) fraction in the gas composition that contains hydrogen. Backfilling the system with an inert gas such as helium is the most commonly used flammability-control approach.

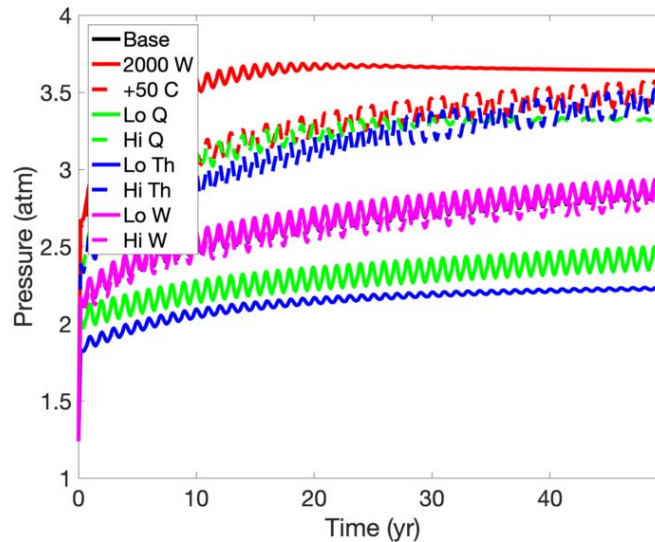


Figure 3-1. Example of Model Results of Pressure Build-up for ATR Fuel Scenario during 50-year Storage [Q = Decay Heat; Th = Oxide Thickness; W = Water Content. See INL/EXT-19-55185]

3. The model makes no distinction between physisorbed water and chemisorbed water, but simply assumes pseudo-boehmite at the maximum water-to-aluminum ratio from literature, that shows some release of water over the initial time periods from the model.
4. This steady-state pressure value is in the same “ball-park” for maximum container pressure as worst-case pressures for a MURR storage container.

3.4 Task 4 – ATR Oxide Characterization. Task Lead: Phil Winston, INL

The following reports have been issued under Task 4 of this TD program:

Aluminum Clad Spent Nuclear Fuel Task 4: Performance of Aluminum SNF in Dry Storage Experiment Test Plan, INL/EXT-18-45861, July 2018, P. Winston.

Aluminum Spent Fuel Performance in Dry Storage Task 4 Objective 1: Initial Characterization of ATR End Box Samples, INL/EXT-18-51230, September 2018, P. Winston, C. Adkins, J. Aguiar, B Hernandez, D. Murray, K. Tolman, A. Winston.

Aluminum Spent Fuel Performance in Dry Storage Task 4 Aluminum Oxide Sampling of ATR Dry-Stored Fuel, INL/EXT-20-58404, May 2020, P. Winston, S. Middlemas, A. Winston, J. Aguiar, X. Liu, K. Tolman.

The characteristics of the oxide layers of actual ASNF materials from the ATR were evaluated in this task. Two separate material conditions were evaluated: 1) the non-fuel, end box region of ATR fuel assemblies; and 2) the non-fuel, fuel plate region of ATR fuel with a long storage history in the CPP-603 basin with poor water quality followed by dry storage in the CPP-603 IFSF.

End Box Material

To acquire information regarding the oxide surface composition of irradiated, pre-dry-storage aluminum fuels components, non-fueled sections were cut from twenty-two discarded ATR end boxes. Five subsamples taken from the population of 22 were analyzed using several techniques to determine chemical composition, morphology and hydration characteristics. The initial analyses confirmed that the chemical

composition of the samples was consistent with that of Al6061. This validates the expectation that the samples were part of the ATR element side plate material, which should be representative of the cladding composition on the individual fuel plates.

Energy Dispersive Spectrometry (EDS) analysis from Scanning Electron Microscopy (SEM) done using two different methods indicated one to four-micron thick oxide layers present on the samples. The oxide thickness result and compositional analysis were corroborated in parallel, using the Plasma Focused Ion Beam (PFIB) instrument while machining surface samples for Transmission Electron Microscope (TEM) crystallographic analysis. X-Ray Diffraction (XRD) analysis using macro-XRD provided a tentative result that the oxide layer was too thin to image, so that measurement using micro-XRD would be needed to get confirmatory information regarding surface composition. An example of the observed typical oxide cross-section is shown as Figure 3-2.

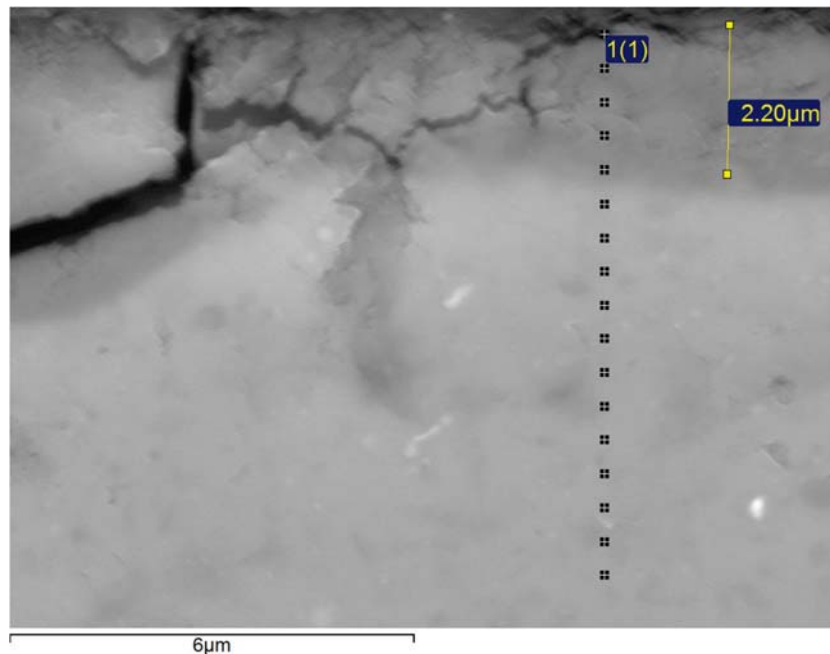


Figure 3-2. SEM of a Typical Oxide Cross-section

Thermogravimetric Analysis (TGA), done in three heating stages from 100 to 300°C yielded indications that negligible mass change occurred in a three-hour period. This suggests that sorbed water is either chemically bound to a degree that greatly inhibits release, or that the oxide layer is sufficiently thin that the released water was below detection by this method. The graphical representation of this measurement is shown as Figure 3-3 for End Box Sample PW-EB-2.

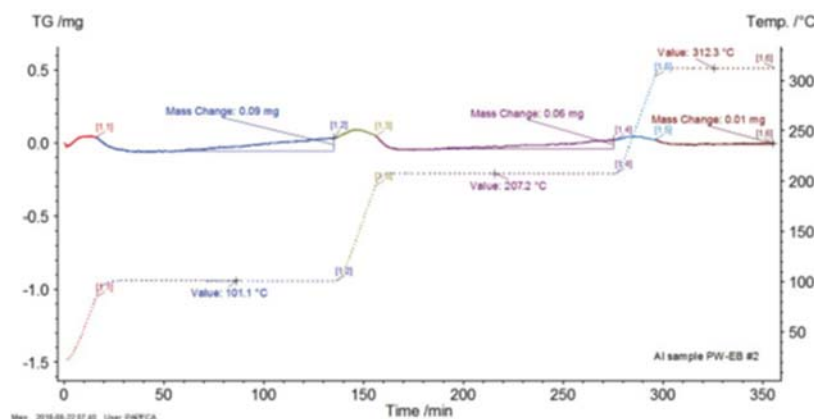


Figure 3-3. TGA of End Box Sample PW-EB-2

When compared to the changes identified in Report HNF-3589 [10] (below) there is no precipitous mass loss when the sample reaches 300°C. Given that the Hanford test was done using a direct temperature ramp-up and the test done on the endbox sample had a one-hour hold time at what would appear to be a critical temperature, there is no indication of a significant hydrated layer that decomposes by 300°C (i.e., a trihydroxide) present on the End Box sample. That is, the monohydrated oxide is the only hydrated oxide that is apparently retained on these materials, as discussed below.

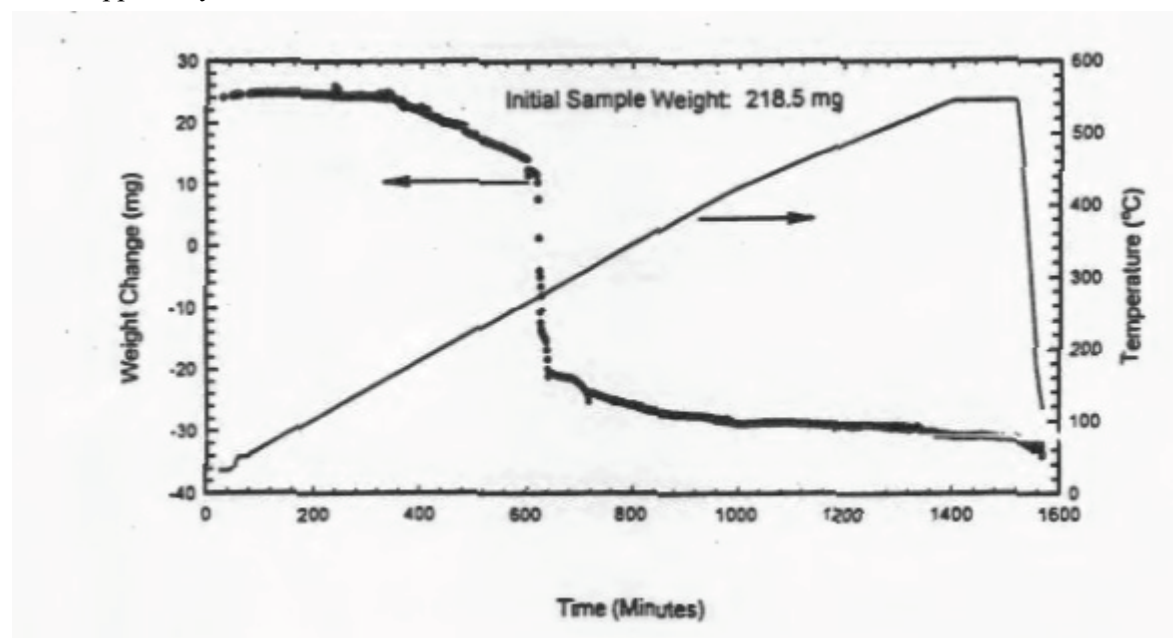


Figure 3-4. Drying Behavior of the Translucent $\text{Al}(\text{OH})_3$ Coating Taken from the Surface of K West Element Stored in Aluminum Canister – from Reference 10.

TEM lamella were prepared in the PFIB handling step but were not analyzed. Only two samples were analyzed using the PFIB instrument, all five were subjected to X-ray diffraction, and two were tested using TGA.

The condition of the oxide layer indicates that limited change has occurred as a result of irradiation and reactor wet storage. This data will be invaluable when comparing samples acquired from aluminum fuel

that has been stored wet in water containing multiple corrosive species, then dried and stored in air for periods in excess of ten years. The characterization of the ATR end box materials (from wet storage in the ATR canal) included the side plates of Al6061 that are the same as the ATR fuel plate cladding alloy in the ATR assembly. Cross-section microscopy showed the oxides on the side plates to be thin (1 to 4 μm), similar to the thickness (2 to 6 μm) of boehmite that is produced in the autoclave treatment of the ATR assemblies prior to their irradiation in the ATR. In addition, insignificant weight loss was observed in these materials with TGA in temperatures up to 300°C. These findings suggest that non-detectable amounts of the gibbsite/bayerite form on the ATR fuel in wet storage following its discharge from the ATR.

ATR Fuel Plate Materials

Oxide materials from ATR assemblies were characterized. The assemblies had a service experience of 13 years of storage in the CPP-603 basin following by 22 years of dry storage in the CPP-603 IFSF. The oxide materials were from two separate sampling schemes: 1) oxide material from scraping from the outer fuel plate (plate 19) of the assembly; and 2) oxide-on-aluminum substrate material from cuttings of the side plate corners.

Characterization of ATR oxides from scrapings from an ATR fuel plate showed the oxide to be predominantly boehmite. Characterization of cut corners and from end plate material showed the oxide to be boehmite with a thickness 2-6 μm , consistent with the pre-film characteristics. That is, no significant changes in the characteristics of the oxide film condition due to the ATR irradiation, wet, and dry storage history were observed.

One feature observed on the ATR assemblies during the sampling campaign is “large white oxide blooms” as shown in the photograph below (Figure 3-5) from the test report. This feature is thought to be the low temperature hydrated oxide product of bayerite/gibbsite that formed at locations where the pre-film protective oxide of boehmite was disrupted. The drying recipe (see Task 5) to be determined from this work would thermally decompose this hydrated oxide resulting in a very small amount of boehmite ($<< 1\%$) in addition to the attendant boehmite on the ATR assembly plates formed from pre-filming.



Figure 3-5. Closeup view of ATR Element Lifted by Side Plate, Showing Corrosion Around Lift Penetration Caused by Friction-type Handling Tool

3.5 Task 5 – Vacuum and Forced Gas Dehydration for Drying ASNF. Task Lead: Rebecca Smith, INL, Travis Knight (and graduate students), USC, and staff from Holtec International

Background R&D information for drying removal of oxide-on-substrate: SRNL LDRD investigation – Principle Investigators Anna d’Entremont and Roderick Fuentes:

An investigation of the thermal decomposition of aluminum hydrated oxides was performed to determine drying behavior of ASNF with attendant oxides. The materials studied were powders of the oxides and as oxides-on-flats (aluminum coupons). The investigation used TGA test methods of laboratory materials. The results are reported in detail in reference 11. Qualitatively, mass loss from a film-substrate showed that mass loss increased with maximum drying temperature for all test temperature conditions similar to the powder tests.

Important findings from the work confirm the literature that complete dehydration of the boehmite would require very high temperature conditions ($\sim 500^{\circ}\text{C}$). The dehydration of the tri-hydrated bayerite film could be practically achieved for ASNF with drying at temperatures slightly above 200°C . Figure 3-6 shows a TGA test result of the thermal treatment of the aluminum with a bayerite film.

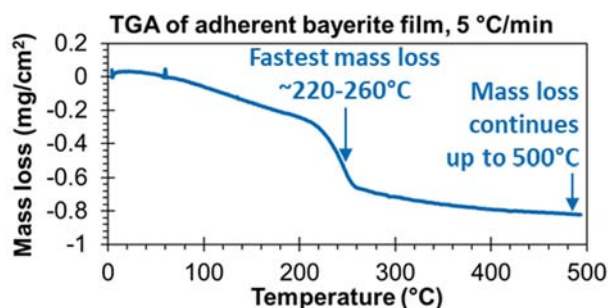


Figure 3-6. TGA of $\sim 8\ \mu\text{m}$ Thick film of Bayerite on an Aluminum Substrate

Aluminum Clad Spent Nuclear Fuel Task 5: Oxide Layer Response to Drying Experimental Test Plan, August 2019, Rev. 1, R. Smith.

Engineering scale drying experiments are planned to be performed in CY20 [12 13]. The experiments will employ mock ASNF assemblies with a limited number of chemically treated aluminum plates to simulate the aluminum hydroxides found on ASNF. The primary goal is to develop an understanding of the removal of free and chemically-bound waters of a prototypic configuration of ASNF-in-canister under thermal conditioning using conventional SNF drying technologies to support development of a drying standard, with technical basis, for packaging ASNF in the DSC.

Physiosorbed and bulk water found in experiments will be dried in the process and the effect on drying operations noted. The design of the experiments includes mock ASNF assemblies that are MTR-design (contain plate fuel elements) with dummy fuel plates with hydrated oxides. A typical testing arrangement of 10 assemblies is loaded into the modified Type 1a Basket design in a 1/3 length size DSC (“short DSC”).

The mock ASNF assemblies are to be fabricated from bolted plates of 6061 aluminum sheet metal. Spacers at each edge will provide the proper gap between plates. Each surrogate assembly is made from a series of twenty $3.15'' \times 0.05'' \times 49.5''$ plates and nineteen pairs of spacers. For the plates, aluminum sheet metal with 16-gauge 6061 aluminum, 0.05082'' thick is used which is similar to ATR plates at 0.05'' thick. Spacers located between sheets at edges to create the plate gap will be fabricated from 12-gauge 6061 aluminum (0.08081'' thick) which is similar to actual the ATR gap of 0.078 inches. The dimensioning was chosen to yield a surface area and metal volume as close to that of the true ATR assemblies as possible.

Two different configurations of the Type 1a Basket have been considered during the initial modeling phase. In the first, a series of “mouse holes” have been cut at the base of the basket walls to promote flow between each slot. Each arc is parabolic, with a width and height equal to one half of the total wall length. The second configuration includes a 2.5” tall “false bottom,” with an array of nine 0.25” (0.635 cm) holes drilled in the floor of the basket.

Modeling of the drying chamber, basket, and mock ASNf assemblies was conducted to estimate temperature distributions throughout the chamber during forced helium drying and over the anticipated drying period. This modeling was used as input to decisions on the design of the test system. Work on modeling continues in the period during setup and testing to develop preliminary drying models. Analysis of experimental results will later be used to validate these and subsequent models.

The hydrated oxide film preparation will result in a ~10 µm layer of bayerite on Al6061 plate substrates. Drying methods for a basket of 10 mock-up ATR cropped assemblies in a short DSC will include vacuum drying and forced helium-gas dehydration (FGD) methods.

The drying chamber is designed to accommodate a single basket layer of ASNf assemblies and be the same 18” external diameter (internal diameter 17.25”) to accommodate the Type 1a Basket. It will be fabricated in two sections joined by a bolted flange.

A target temperature of 220°C has been achieved for the maximum hold times (12 hours) in the test matrix for FGD.

A preliminary hold time of 4 hours for a target temperature of 220°C has been suggested as a drying treatment. This drying treatment is expected to decompose the hydrated oxide systems of bayerite/gibbsite. Large plate radiolysis testing (described below) has used this thermal treatment recipe.

Results to date support the preliminary conclusions that ASNf can be dried with FGD sufficiently to minimize the impact of the radiolysis of any bound waters.

3.6 Task 6 – Oxide Formation and L Basin Specimen Characterization. Task Leads Anna d’Entremont, Luke Olson, Roderick Fuentes, Chris Verst, Kallie Metzger, SRNL.

Aluminum Clad Spent Nuclear Fuel Task 6: Surrogate Sample Preparation and Validation Experiment Test Plan, INL/EXT-18-45864, July 2018, M. Connolly.

Preparation of Aluminum Oxide Films Under Water Exposure – Preliminary Report on 1100 Series Alloys, SRNL-STI-2018-00427, Rev. 0, August 2018, K. Metzger, R. Fuentes, A. d’Entremont, L. Olson, R. Sindelar.

Preparation of Aluminum Oxide Films Under Water Exposure – Preliminary Report on 6061 Series Alloys, SRNL-STI-2018-00449, Rev. 0, August 2018, A. d’Entremont, R. Fuentes, L. Olson, R. Sindelar.

Characterization of Oxyhydroxides on a Dry-Stored Fuel Plate From L-Basin, SRNL-STI-2018-00428, Rev. 0, October 2018, L. Olson, R. Fuentes, A. d’Entremont, R. Sindelar.

Preparation of Aluminum Oxide Films Under Water Exposure – Preliminary Report on 5052 Series Alloys, SRNL-STI-2018-00646, Rev. 0, November 2018, A. d’Entremont, R. Fuentes, L. Olson, R. Sindelar.

Characterization of Oxide Films on Aluminum Materials following Reactor Exposure and Wet Storage in the SRS L-Basin, SRNL-STI-2019-00058, March 2019, L. Olson, C. Verst, A. d'Entremont, R. Fuentes, R. Sindelar.

This task had two primary subtasks:

- Development of oxide formation protocol for laboratory testing specimens to be used as surrogate materials for subsequent radiolysis and corrosion testing (demonstrate surrogate materials are representative of the hydrated oxide films on actual ASNF materials).
- Characterization of the oxides on actual aluminum cladding materials exposed in-core followed by extended wet and dry storage.

Oxide Formation

Part of the Task 6 activities was to perform laboratory experiments to produce hydroxide (oxide) films on Al6061 series alloy substrates immersed in water at controlled temperatures.

The general observations and findings are summarized as:

- 1) Trihydroxide films of gibbsite/bayerite were the predominant types formed in hot-wall exposure at 50°C. The weight gain was approximately 10.8 $\mu\text{g}/\text{mm}^2$ of corroded specimen area for a 31-day exposure. The observed film thickness ranged from approximately 1 to 2 μm , depending on the local region examined.
- 2) Boehmite film was the predominant type formed in hot-wall exposure at 100°C. The weight gain was approximately 1.14 $\mu\text{g}/\text{mm}^2$ of corroded specimen area for a 29-day exposure. The observed film thickness of specimens immersed in 100°C water for 12 to 41 days ranged from approximately 0.5 to 2 μm , depending on the local region examined. The oxide films from the hot-wall tests were subject to additional growth post-hot-wall test during wet storage in room-temperature water. This is attributed to the hot-wall formed oxides being nonprotective compared to the intentional “pre-film” oxides and allowing continued corrosion to occur.
- 3) “Pre-filming” exposures in 185°C liquid water were performed to compare to the pre-filming practice used for ATR fuel. The weight gain of Al6061 samples from 9 to 72 hours were well fitted by a power-law model ($W=b \exp(-c/T) t^2$). Some of the results are shown in Figure 3-7 and model components derived from the curves are listed in Table 5.
- 4) Exposure to the ATR pre-film time of 18 hours yielded an estimate oxide thickness of 2 microns on the 6061 sample, consistent with ATR reported results of 2.3 μm .

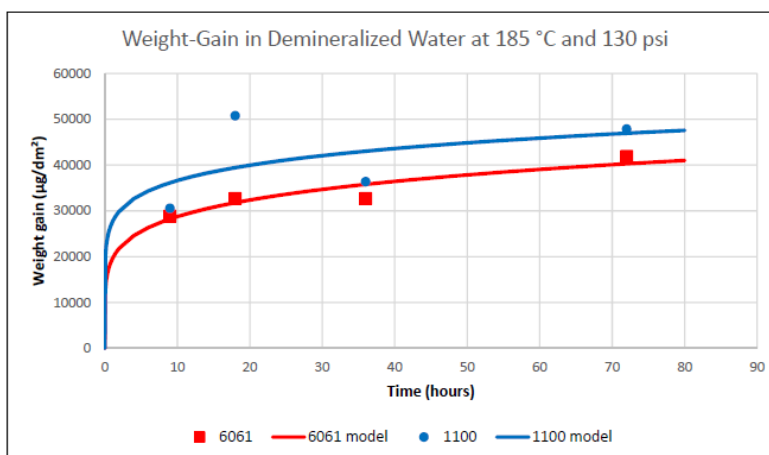


Figure 3-7. Weight Gain per Unit Area for Specimens Immersed in 185°C Liquid Water as a Function of Exposure Time.

Table 5. Fitted Parameters and R^2 Values for the Weight Gain Data in Figure 3-7 According to Power Law Model with Temperature $T=458$ K.

	6061	1100
b	3.301×10^6	3.301×10^6
c	2352	2194
z	0.1707	0.1256
R^2	0.85	0.25

Irradiated Fuel Oxide Characterization

Characterizations were made of films from actual ASNF materials with service experience of in-reactor and post-discharge storage in L Basin up to 50 years.

Characterization of oxide films was performed on:

- RU-1 (Uruguay reactor) fuel plate end tab of Al6061. This fuel had been several decades in uncontrolled dry storage,
- MURR end fitting of Al6061 stored in L Basin,
- Mark 16-B (SRS production reactor assembly) end fitting of Al6063 stored in L Basin,
- Universal Sleeve Housing (USH) for the SRS production reactor assemblies of either Al6061 or Al6063 stored in L Basin.

The films from actual ASNF materials (cladding and end-fitting components of an ASNF assembly) have shown a multi-type layer of oxides. Figure 3-8 shows the microstructures of oxides on the surface of ASNF materials from the SRS L Basin (MURR, USH, Mk-16B) and a dry storage drum (RU-1). The film characteristics (type and film thickness), and the corresponding service exposure conditions are detailed in the program reports. The maximum oxide film thickness observed in the dry-stored fuel is bounded by 25 μm ; the maximum oxide film thickness observed in the wet-stored fuel the included a range of in-reactor and post-discharge service conditions is bounded by 15 μm .

Based on the comparison of the oxide peaks, known operation histories, length of time in wet storage, and assuming oxide formation in the storage pool has not dominated the oxide formation on the samples, it can be surmised that the USH was exposed to the highest, boehmite-forming temperatures, followed by the MURR, and lastly the Mark-16B which had the lowest temperature exposure.

Characterization of the as-received oxides included the oxide morphology, thickness, structure, and chemical composition.

The results of the characterization include:

- XRD analysis revealed both bayerite ($\text{Al}(\text{OH})_3$) and boehmite ($\text{AlO}(\text{OH})$) on the surface of the MURR and USH samples, and bayerite, boehmite, and gibbsite ($\text{Al}(\text{OH})_3$) on the surface of the Mark-16B sample. The presence of the bayerite on the USH, which is believed to have operated close to 90°C, suggests that further oxide growth in wet storage needs to be accounted for, despite the apparent protectiveness of the 185 °C pre-films.
- Comparison of the ratios of boehmite and bayerite XRD peaks indicates the USH had the highest exposure temperatures with the most boehmite being formed, followed by the MURR. The Mark-16B had the least boehmite detected. Estimated sample histories based on reactor documentation supports these conclusions.
- Results of planview SEM are shown in Figure 3-8.
 - i) the MURR oxide thickness was ~5 to ~10 μm ,
 - ii) the Mark-16B oxide thickness was ~5 to ~15 μm .
 - iii) the USH oxide thickness was indiscernible in cross-section with the mounting method performed and SEM capabilities available (although it was detected in plan-view and by XRD),
 - iv) the surface oxide morphology from plan-view of the MURR sample appears blocky and dense, which is expected to be more protective than a porous film,
 - v) the surface oxide morphology from plan-view of the USH appeared globular and dense, which is expected to be more protective than a porous film,
 - vi) The surface oxide morphology from plan-view of the Mark-16B primary oxide appeared blocky but porous. When the thick oxide fractured off near the edges of the sample from cutting, it appeared a uniform thin oxide was present.

From the current data a nominal-high oxide thickness value of about 15 μm is suggested.

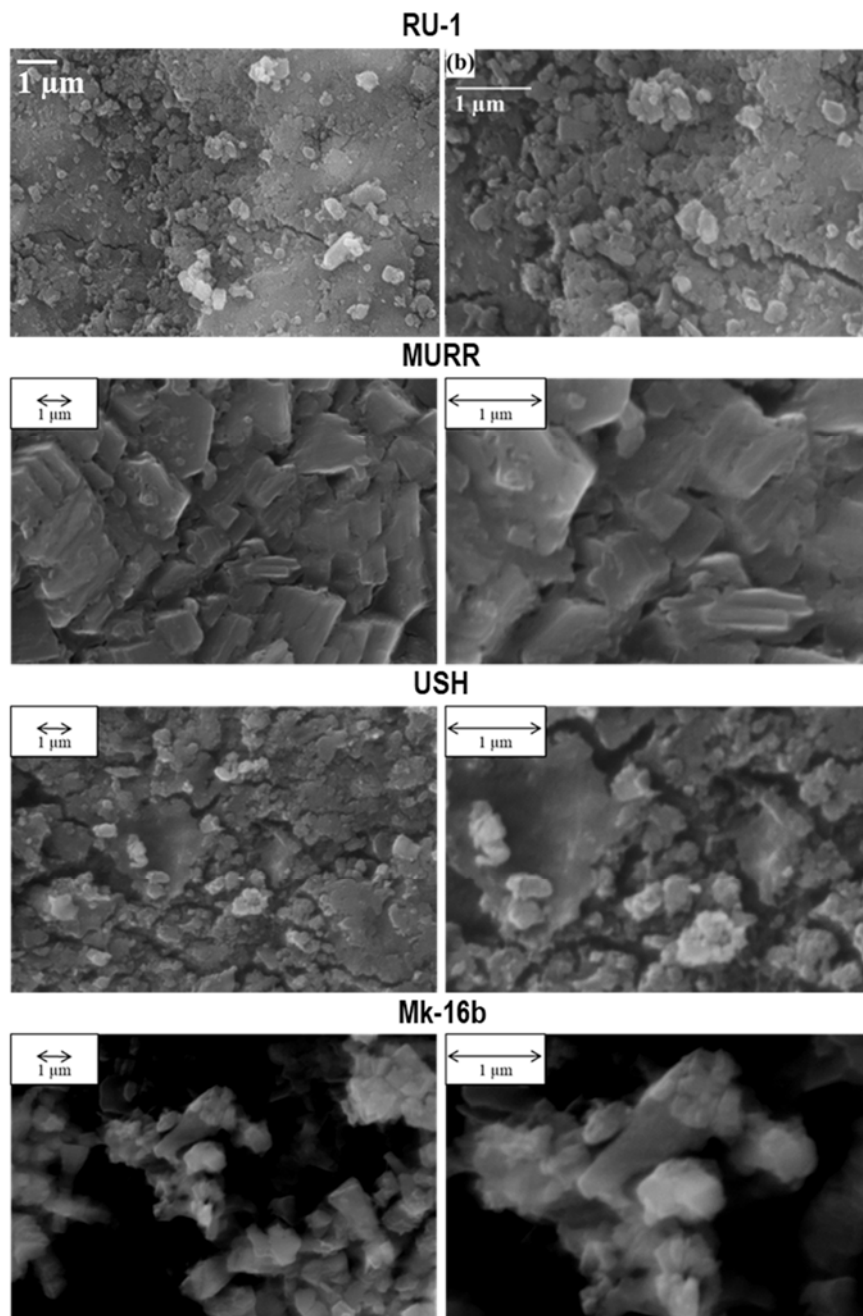


Figure 3-8. Scanning Electron Microscopy Micrographs of the Surfaces of ASN Materials from L Basin at SRS [14]. Mixed Types of (Oxy)Hydroxides (bayerite/gibbsite and boehmite) were Observed in the Films.

Summary of Results

Observations and results are:

- Hydrated oxide films on aluminum substrates were prepared as surrogates for ASN materials for further corrosion and radiolysis testing. The type (bayerite/gibbsite; boehmite) and the morphology (clumped rods/platelets; blocks) of the hydrated oxide films are dependent on the water immersion conditions (temperature, time, water quality).

- The hydrated oxide films on actual ASNF materials with an irradiation and storage exposure were characterized in terms of type, oxide morphology, and oxide film thickness.
- Except for oxide film thickness which is a time-dependent growth process, the surrogate specimens can be matched in type and morphology to the actual ASNF materials. The hydrated oxide film thickness of the actual ASNF materials were not uniform across the cm-length specimens.

The predicted values to characterized values of oxide thickness for the specimens removed from L Basin are shown in Table 6.

Table 6. Oxide Thickness Summary and Comparison to Values Derived from Literature Models

Sample	Predicted range* (μm)	Observed Range (μm)
MURR	4-5	5-10
USH	2-16	ND
Mark-16B	0-19	5-15

* Origin of predicted values are discussed in the task reports. Some predicted values are extrapolations and are given for estimation purposes only.

ND: Not detected in cross-section in SEM

4.0 Instrumented Lid

A proposed follow-on activity to laboratory studies described in this document is to monitor dry storage behavior of ASNF in a sealed and instrumented canister. Monitoring the performance of ASNF in a sealed and instrumented canister provides an opportunity to: (1) evaluate the appropriate technologies for potential long term monitoring, (2) collect canister environment conditions as soon as possible, (3) evaluate the effectiveness of drying process and technologies, (4) confirm welding techniques for leak tightness, (5) verify and validate current laboratory-based study results and analytic modeling approaches, and (6) provide additional dry storage options for ASNF at the INL site. Therefore, an instrumented lid was designed and tested for the purpose of deployment in an extended demonstration of up to 10 years. The Lid is designed to be deployed on an 18" diameter DSC.

4.1 Design Requirements

The requirements for a system to monitor and analyze the environmental conditions of ASNF in dry storage was given in reference 15. The system would be composed of a custom canister assembly and a modular instrument manifold, to monitor the temperature, humidity, pressure, gas composition with minimum detectable level of 500 ppm, and gas space entrained particle (if any) radioactivity.

The design of the lid is based on the design of the 18" Outside Diameter Spent Nuclear Fuel Canister (short) [16] and is designed to be compatible with lifting components. The Lid is designed to be compatible with final sealing of the canister after the 10-year monitoring period.

4.2 Instrumented Lid System Components

The instrumented Lid System is comprised of several components shown in Figure 4-1; the canister lid, the connecting plate, the instrumentation manifold, and a custom Type 1a basket. The lid is compatible with the canister and provides sampling access in the normally sealed system. The connecting plate allows the instrumentation manifold to connect to the lid sampling ports and is intended to allow engaging and disengaging to the canister remotely. The instrumentation manifold contains the measurement system and is designed to be located in a low dose area. The custom basket allows for the insertion of gas piping and

thermowells into the canister acting as a guide for lid installation and assures the measurement hardware does not interfere with the loaded fuel.

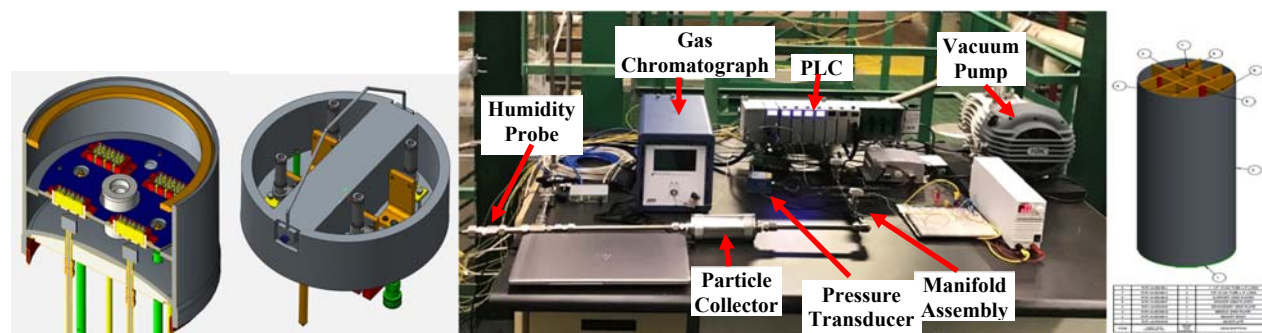


Figure 4-1. Instrumented Lid System Components Including; a) Canister Lid, b) Connecting Plate, c) Instrumentation Manifold, d) Modified Type 1a Basket

4.3 Instrumentation System

The gas, temperature, pressure, and particle collection instrumentation are integrated into a gas manifold and controlled by a programmable logic controller (PLC) and logged on a data acquisition (DAQ) system.

A sample from the canister is obtained by evacuating the manifold and opening a valve accessing the canister through gas sample penetration in the canister lid. The gas sample will pass into the cascade impactor for particle scrubbing and particle analysis. The first function will protect other sensitive equipment from harmful particles which may have escaped from the canister as a result of corrosion or oxide spallation. The latter function will provide the means to identify and characterize any corrosion products or particulate matter carried in the gas stream from the canister.

Gas composition analysis will be performed with a micro gas chromatograph (GC) in a low background location away from the canister. Analysis will target Hydrogen, Oxygen, and Nitrogen. Humidity measurements will be performed with a Humidity/Temperature Probe. Efforts will be made to avoid condensation, on the system tubing. Pressure measurement will be performed using a pressure sensor.

After sampling is completed, the remaining gas will be filtered through a HEPA filter and exhausted or recirculated into the canister through the secondary valve. All information from these systems will be collected by the DAQ system and logged into a computer for further analysis.

4.4 Instrumented Lid Data

The data generated by the Instrumented Lid system will be used to monitor the condition of ASNF over the course of several years. The system provides real-time data on temperature, pressure, gas composition and relative humidity. This data is intended to be used to evaluate the effects of dry storage on ASNF and how the gas composition changes over time. Information will be used to compare trend predictions from the modeling and allow for extrapolation of canister conditions.

5.0 FY21 EMTD Continuation Activities

Radiolysis Testing – Laboratory and Actual ASNF Material Testing

The FY21 activities will provide experimental data on the radiolytic gas generation from the hydrated oxide layers on ASNF surrogates, and actual ASNF claddings, service-experienced from reactor and post-discharge wet storage.

The radiolysis testing to date has shown that physisorbed water vs. chemisorbed water discrimination, dose levels to develop G-values, and the steady-state gas concentrations of a hydrated oxide system under radiolysis is difficult to interpret. In addition, there has been no radiolysis data on post-dried oxides. For these reasons, additional testing in CY20 have been planned.

The activities of this are under two subtasks. The two subtasks are:

- Subtask 1: Evaluation of physisorbed vs. chemisorbed radiolytic gas yields from aluminum hydrated oxides-on-aluminum, before and after drying treatment,
- Subtask 2: Evaluation of radiolytic gases yield from service-experienced ASNf materials, before and after drying treatment.

The primary objectives of subtask 1 are to distinguish initial radiolytic gas yields rates or “G-values” from separate and combined physisorbed/chemisorbed waters on (laboratory-grown) hydrated oxides-on-aluminum materials.

The primary objectives of subtask 2 are to provide testing to verify the results from actual service-experienced ASNf materials are consistent with laboratory-grown materials.

The results from subtasks 1 and 2 under a common test protocol will enable a direct comparison of laboratory-prepared hydrated oxides to those from actual service-experienced hydrated oxides, both before and after a selected drying treatment.

Two regimes of radiolytic gas production from hydrated oxides-on-aluminum are postulated: 1) the low-dose regime where the forward reaction and “G-value” determination is made; and 2) the high-dose regime where a steady-state radiolytic gas concentration in a system in a radiation field would exist. The results from this testing will characterize this trend in radiolytic gas concentration with absorbed dose.

Radiolysis Testing – Large Plate, Instrumented On-line Monitoring and Model Verification

Previous radiolysis studies performed under Task 2 of the action plan have established baseline estimates of hydrogen generation rates from the hydrated oxides [1]. These tests provided insight to initial hydrogen “G-values” for corroded and uncorroded samples and allowed for general trend interpolation between the low and high dose points. The need for dozens of individual samples limited the number and maximum irradiation time of high dose samples. This lack of initial convergence at low dose and sparsity of data at high dose are both addressed in the planned Instrumented Lid testing in CY20.

Increasing the amount of coupon surface area under irradiation and coupling to the Instrumented Lid system will provide improved data on the transient behavior of the radiolysis of the hydrated oxide layers present on the surfaces of aluminum. This Instrumented Lid test will have the benefit of measuring and analyzing real time conditions of radiolytic gas generation from a single continuous sample irradiation period with adjustable sampling frequency to prioritize resolution at low doses. Additionally, the very large sample surface area, relative to previous tests, is expected to more quickly yield the anticipated “high dose” hydrogen equilibrium concentration. Lastly, this large sample testing in a helium filled steel vessel provides a defensible analogue for future loaded DSC and is the logical precursor to deployment and further testing with ATR fuel.

Experimental work is currently underway to investigate the radiolytic gas yields of scale-up amount of surrogate ASNf in a small chamber vessel. The surrogate materials have aluminum hydrated oxides that were grown for over 30 days in distilled water at room temperature. The samples are currently being irradiated in sealed vessels with a helium atmosphere, and radiolytic hydrogen generation rates are being measured. Two test vessels are being irradiated, one with a drying treatment and the other without, to evaluate the change in radiolytic gas yield between the two conditions. To dry the test assembly, it was

placed into an oven at 220°C and held for 4 hours. The vessel was then put under vacuum and purged prior to blanketing with helium.

Preliminary results show that the undried coupon assembly is generating hydrogen at a linear rate as shown in Figure 5-1.

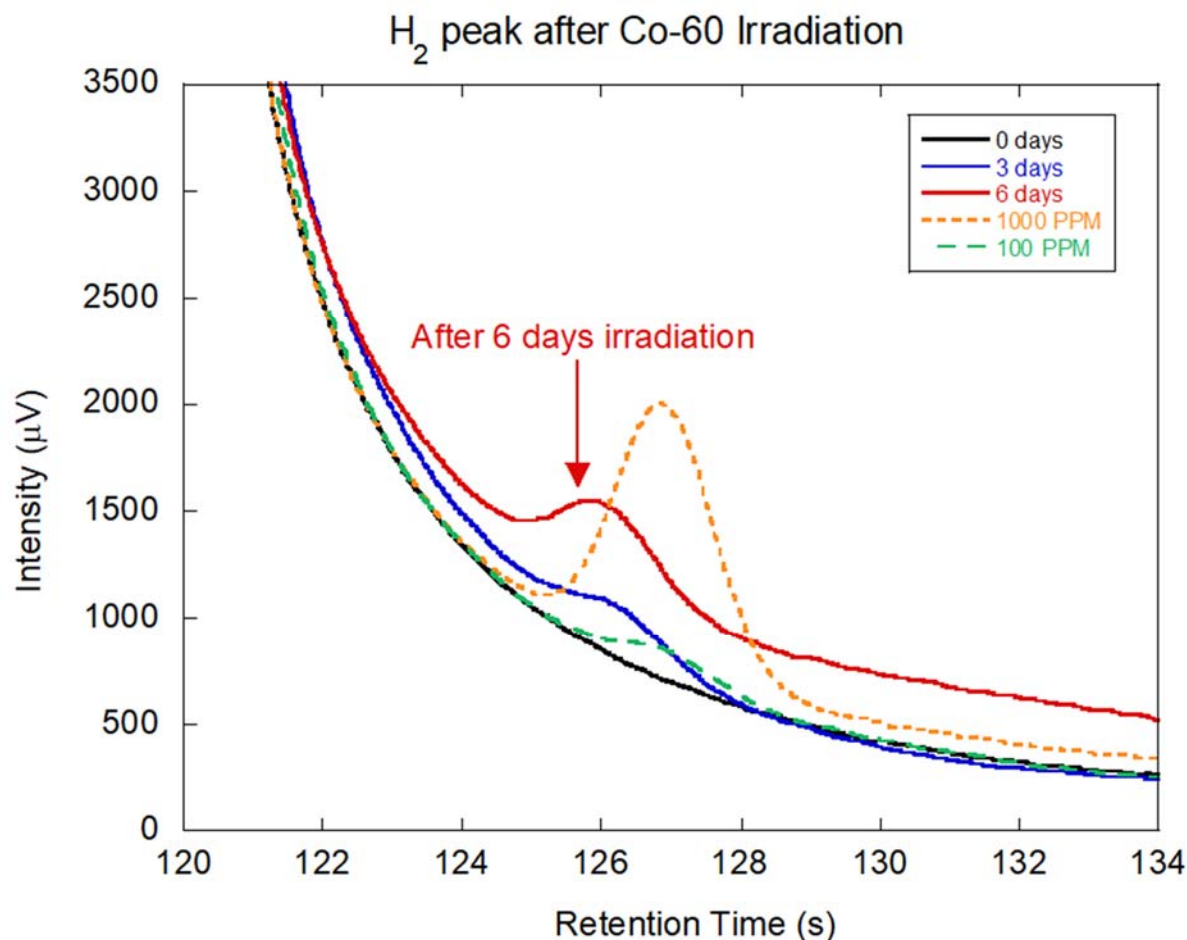


Figure 5-1. Gas Chromatograph Curves (solid lines) Corresponding to H₂ Gas Generation after 0, 3, and 6 Days of Co-60 γ Irradiation. Calibration Curves for 100 PPM H₂ (dashed line) and 1000 PPM (dotted line) Are Plotted for Reference

The preliminary results for the test assembly that underwent the drying treatment have thus far shown a very negligible hydrogen peak (above detection limit, but too low for the software to integrate and quantify) for the comparable time period.

The data generated will be provided for comparison to the analytic modeling methods (Task 3) [2] and serve as proof of concept for a potential future full-scale Instrumented Lid deployment.

6.0 Conclusions

This interim status report provides a summary of the task-based tests and analysis activities conducted under the EMTD program to fill the information gaps and complete the technical bases for extended (> 50 years) dry storage of ASNF.

The overall conclusions from this technology development program including the anticipated successful completion of FY21 activities, are that:

- The testing and analysis results of the characterization of ATR fuel, and the performance modeling in its storage configuration, show that the ASNF presently in vented interim dry storage (IFSF) is safe for continued, extended dry storage (> 50 years) without corrosion degradation challenges;
- The testing and analysis results of ASNF from L Basin can be safely placed in sealed canister storage without corrosion degradation, canister pressurization, and canister flammability challenges pending ultimate disposition;
- The ASNF-in-canister performance modeling, including the H₂ generate rate inputs from extensive radiolysis testing of hydrated oxides on aluminum substrate testing allows reliable performance prediction of configurations of ASNF-in-canisters including parameters of temperature, gas space evolution, and canister pressurization.

The primary findings from the separate tasks completed to date are:

Task 1 – Hydrated Oxide Layer Growth Behavior

The aluminum hydrated oxide chemistries and behaviors under corrosion conditions were analytically modeled and tested. The behaviors are well understood with conventional chemical thermodynamics formalism. Testing with carefully controlled temperature and humidity exposure conditions to quantify oxide film growth and hydrogen release show the attendant (existing) hydrated oxides limit additional corrosion under bounding conditions of expected storage. This task is completed.

Task 2 - Oxide Layer Radiolytic Gas Generation

First-time data on radiolytic yield from hydrated oxides on aluminum substrates were developed. The data included several cover gas, temperature, and relative humidity conditions. The data applied to the analytic model (Task 3) enables gas composition and pressure condition predictions for specified cases of the ASNF-in-canister. Additional testing (in progress, to be completed in FY21) is necessary to: 1) distinguish physio- and chemisorbed contributions to hydrogen generation; 2) establish forward reaction hydrogen generation regime vs. regime influenced by back-reactions; and 3) evaluate the impact of helium cover gas on radiolytic hydrogen generation. Additional radiolytic data from residual hydrated oxides, post-thermal exposure, commensurate with a drying treatment to remove the low temperature hydrated oxides, is in progress.

Task 3 - Sealed and Vented System Episodic Breathing and Gas Generation Prediction

Integrated coupled-chemical, 3D multi-physics CFD models and simulations were constructed for:

- The (vented) canister chemical system to represent the CCP-603 IFSF conditions. The results of this modeling for an additional 50 years of storage show no adverse impact to the fuel that would preclude its readily handling and placement in a sealed DSC in road-ready storage.
- The DSC (sealed) canister (ASNF-in-canister) chemical system including the radiolytic gas generation. The results of this modeling show that even at the bounding conditions of hydrated oxide film thickness, and high rate of radiolytic yield of hydrogen from the ASNF, the canister pressure is well-within design capacity. The results also show that the oxygen concentration (10⁻⁸ volume percent) provides clear oxygen-limited conditions to preclude flammable conditions in the canister.

Additional modeling of the scale-up (large plate) radiolysis testing of hydrated oxide aluminum in small chambers is an activity in FY21.

Task 4 - Performance of ASNF in Dry Storage

End-box fittings of ASNF from the ATR that have a water-storage history in the ATR canal, and scrapings of ATR that have a dry storage service history have been characterized.

The ATR end box materials (from wet storage in the ATR canal) included the side plates of Al6061 that are the same as the ATR fuel plate cladding alloy in the ATR assembly. Cross-section microscopy showed thin (1 to 4 μm) oxides of boehmite, similar to the thickness (2 to 6 μm) of boehmite that is produced in the autoclave treatment of the ATR assemblies prior to their irradiation in the ATR. No evidence of gibbsite/bayerite was found in thermal gravimetric testing.

Characterization of ATR oxides from scrapings from an ATR fuel plate showed the oxide to be predominantly boehmite. Characterization of cut corners and from end plate material showed the oxide to be boehmite with a thickness 2-6 μm , consistent with the pre-film characteristics. That is, no significant changes in the characteristics of the oxide film condition due to the ATR irradiation, wet, and dry storage history were observed. This task has been completed.

Task 5 - Oxide Layer Response to Drying

A 1/3 scale mockup of a DOE standard canister and basket with in-canister drying testing via (a) forced gas (helium) dehydration and (b) vacuum drying is in progress. Test execution is in progress at a commercial vendor site with the University of South Carolina partners. Thermal modeling is performed to evaluate the temperature and drying conditions is part of this task. The drying testing to date used FGD and has demonstrated ability to achieve temperatures of nominally 220C in excess of several hours; this is expected to enable thermal decomposition of the gibbsite/bayerite oxide to result in dried ASNF-in-canister that would have a nominal remaining hydrated oxide (amorphous boehmite) content.

Task 6 – Oxide Formation and L Basin Specimen Characterization.

One subtask under this task was to performed water immersion experiments to produce the hydrated oxide films on fuel cladding aluminum alloys (1100, 5052 and 6061) that are formed at low (< 80C) and high (>80C) temperature conditions. The characteristic oxide morphologies, thicknesses and chemical compositions were determined for use in preparing additional specimens for testing under the other program tasks.

The second subtask under this task was to characterize actual irradiated and service-experience aluminum cladding materials with a long term (up to 50 years) storage history. Detailed characterization of the hydrated oxide films of 4 separate aluminum material conditions has been completed. The bounding oxide thickness of 15 μm was observed. This task has been completed.

Instrumented Lid Task

A special instrumented lid system to provide gas space sampling and temperature monitoring of SNF in dry storage in the DSC has been designed, fabricated and tested. The lid system is composed of the following: a DSC fuel basket; a lid assembly (ported lid and mating top hat); and an instrument manifold to accommodate gas-sample sensors. The complement of lid sensors will be used to monitor DSC internal conditions include temperature, humidity, pressure, gas composition, and particle collection.

Path Forward - Several additional activities are continuing in FY21. The in-progress activities address information gaps identified in studies completed to date, resolve some questions such as effect of physisorbed vs chemisorbed water effects on radiolytic yields, establish steady state G values, and establish a preliminary drying procedure. The results of these additional studies will reduce uncertainty and conservatism in modeling/simulation results of extended performance. The tasks continuing into FY21 include: 1) the completion of the FGD and the vacuum drying appropriate scale-up drying test campaign to investigate drying approaches for a charge of mock full-scale ATR assemblies prepared with an inventory of hydrated oxides in a one-basket level, 1/3-size DSC (Task 5 activity); 2) additional radiolysis testing of coupons to investigate high dose conditions (steady-state) and further evaluate cover gas (helium) effects; the radiolysis coupon testing will include additional L Basin aluminum cladding with mixed hydrated oxides, before/after a drying treatment (Task 2 activity); 3) Following completion of additional radiolysis testing in Task 2, the G-values will be used to update the model results for ATR and similar SRS fuels in DSC; and 4) radiolysis testing of large plate of simulated ASNF fuel plate with a hydrated-oxide layer, before/after drying treatments for long-term monitoring using the instrumented lid sensor system (Task 2, Task 3, and Instrumented Lid activity). The large plate testing will include the coupled-chemical system modeling of the mini-canister system as developed in Task 3 of the EMTD (model validation of hydrogen generation).

Following the completion of the laboratory activities in FY21, the next step for dry storage technology readiness is hot demonstration (unfunded) to provide verification of the ASNF behavior results, and validation that the ASNF-in-DSC can be implemented for a road-ready disposition for ASNF.

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