PNNL-30701

Independent Technical Review of INL Aluminum-Clad Spent Nuclear Fuel (ASNF) Oxide Layer Radiolytic Gas Generation Resolution

Task 2

October 2020

EC Buck
RS Wittman
BD Hanson

Prepared for the U.S. Department of Energy
under Contract DE-AC05-76RL01830

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Pacific Northwest National Laboratory
Richland, Washington 99354

Summary

PNNL staff performed an independent technical review (ITR) of the aluminum-clad spent nuclear fuel (ASNF) program Task 2. The objective of Task 2 is to determine *G*-values for the radiolytic production of gaseous molecular hydrogen (H_2) from the aluminum oxyhydroxide layers present on ASNF cladding. The *G*-values need to be defensible, bounding, but not overly conservative. As part of the ITR, the team reviewed program documents, Task 2 work plans, and results to date. In addition, the team held three separate video conferences with the program research staff to ask clarifying questions and obtain additional detail. The PNNL ITR team concludes that if the program follows the methodology and rigor outlined in the test matrices, the program will develop *G*-values for a defensible technical basis of extended storage of ASNF.

Specifically, the ITR team:

- Agrees that testing of corrosion layers on aluminum coupons is appropriate and testing of powders is not needed.
- Agrees that future work should focus on radiolytic studies in a helium environment, as it is anticipated that the standard DOE spent fuel canisters will be back filled with helium.
- Supports the proposal to test scrap coupons from L-Basis, especially if the scraps are an alloy other than Al-1100 or have corrosion layers thicker than 5 µm.

The ITR team has the following recommendations that would increase confidence in the test results and overall program:

1. The ASNF program should continue to publish results in the open literature.
2. The program should report *G*-values in both traditional and SI units to avoid confusion and to provide a quick check that conversions were done properly.
3. One or more tests should be performed at both INL and SRNL under identical conditions to understand any uncertainty or bias and provide confidence in results.
4. To provide assurance that dose rate is not a factor in determining the *G*-value, the test(s) suggested in #3 should be run to the same accumulated dose and compared.
5. The ASNF program should avoid stating that an objective of the program is to study or develop mechanistic explanations of radiolytic gas generation.

The ITR team determines that the following recommendations are critical and necessary to meet the program objective with confidence and defensibility:

6. The program should perform at least some scoping tests on Al-6061 under the same conditions as Al-1100. If significant differences in H_2 generation are observed, the alloy with a more bounding *G*-value should be the focus of continued testing.
7. A more concentrated effort to link the tested specimens to the actual ASNF cladding and corrosion products should be made. Specifically, the effect of increased corrosion layer thickness and of larger scales should be investigated.
8. More detailed surface characterization, specifically the surface area of the corrosion rind of the specimens before and after irradiation is needed.

9. Scoping studies of irradiations at temperatures of ~165°C and ~175°C should be performed to better understand the significant (3-4-fold) increase in H_2 generation observed at 200°C.

Following these recommendations, most of which are part of the original test matrix proposed by Zalupski (2018), will enable the well-qualified research team to reach the program objective and provide a defensible technical basis for extended storage of ASNF.

Acknowledgments

The authors appreciated the ready interchange of information with the Task 2 researchers, especially Elizabeth Parker-Quaifer and Gregory P. Horne of INL for describing their results and walking us through their methodology. We thank the INL project management team of Josh Jarrell and Michael Connolly for their support and for facilitating the discussions. This contributed to an efficient and enjoyable review process and helped produce a successful review outcome. Finally, we thank the support of Anna Schutz and Tom Brouns at PNNL for helping manage the project.

Acronyms and Abbreviations

AFM	Atomic Force Microscopy
ASNF	Aluminum-Clad Spent Nuclear Fuel
ATR	Advanced Test Reactor
DFT	Density Functional Theory
DOE	U.S. Department of Energy
EBSD	Electron Backscattered Diffraction
EM	Office of Environmental Management
eV	electron volt
HFIR	High Flux Test Reactor
iDREAM	Interfacial Dynamics in Radioactive Environments and Materials
INL	Idaho National Laboratory
ITR	Independent Technical Review
MTHM	Metric Tonnes Heavy Metal
MURR	University of Missouri Research Reactor
NNSA	National Nuclear Security Administration
ORNL	Oak Ridge National Laboratory
PNNL	Pacific Northwest National Laboratory
SEM	Scanning Electron Microscopy
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
TEM	Transmission Electron Microscopy
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction

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1.0 Introduction and Scope of Review

Staff at Pacific Northwest National Laboratory (PNNL) has been tasked with performing an independent technical review (ITR) of portions of the Aluminum Clad Spent Nuclear Fuel (ASNF) program led by the Idaho National Laboratory (INL). The objective of the ASNF program is to develop the technical basis for safely storing ASNF for extended (i.e., greater than 50 years) periods. The ITR focused on examination of two of the five tasks of the program and concluded that the methodology and work being performed, especially if the recommendations made by the ITR are implemented, will provide the data and models necessary to determine if the current plans facilitate extended storage of ASNF.

1.1 Overview of ASNF

Research reactors and high-power or high flux test reactors, such as the Advanced Test Reactor (ATR) at INL and the High Flux Isotope Reactor (HFIR) at Oak Ridge National Laboratory (ORNL), have traditionally used highly enriched uranium fuel in aluminum cladding. The Department of Energy (DOE) Office of Environmental Management (EM) is responsible for managing most of the spent fuel from these reactors until final disposition.

INL currently has ~2.3 metric tons heavy metal (MTHM) ASNF in vented dry storage with an additional ~0.3 MTHM ASNF in wet storage that is scheduled to be moved to dry storage by 2023. ATR generates an additional ~0.08 MTHM/yr that will be stored dry. The Savannah River Site (SRS) currently has ~7 MTHM ASNF in wet storage and continues to receive ASNF from ORNL and various National Nuclear Security Administration (NNSA) programs.

The aluminum clad fuel is fabricated from different alloys, namely 1100, 5052, 6061, and 6063, with 6061 being the most predominant as it is used in fabricating fuel for ATR and HFIR. The alloys differ in the quantity and type of alloying elements; for example, Al-5052 has ~2.5% magnesium, Al-6061 has ~1.0% magnesium and ~0.6% silicon, whereas Al-1100 is commercially pure aluminum. All these alloys react with water both during reactor operations and wet storage to form various oxyhydroxides. The oxyhydroxide formed (e.g., gibbsite, boehmite, and/or bayerite) is dependent on the temperature and water quality during reaction as well as the alloy type. The oxyhydroxides differ in structure, the amount of water in the hydrated oxide, as well as the amount of water that may be trapped or physisorbed in the oxide layer. Each oxyhydroxide decomposes and releases water at different temperatures. Residual water remaining after drying, whether chemisorbed or physisorbed, may result in additional corrosion of the fuel, cladding, or canister, or undergo radiolysis which could result in molecular hydrogen (H_2) or other gas generation which in turn could result in canister over pressurization or flammability conditions.

1.2 Overview of ASNF Program

The current ASNF inventory is stored in both wet and dry conditions. Given the limitations on aqueous reprocessing and delays in a high-level waste repository, dry storage of ASNF is expected for extended periods of time, significantly longer than originally planned. With no active repository program, the program is planning on extended storage potentially for greater than 50 years. The ASNF from ATR is currently stored in vented or unsealed canisters in the INL CPP-603 building. Vented storage means the lids are simply set on the canister and not bolted and no O-ring in place. These vented canisters are not transportable or “road-ready”. All

ASNF not reprocessed will eventually have to be in sealed and inerted (i.e., filled with inert gas) canisters that are transportable.

In response to gaps and technical needs identified by the DOE Spent Nuclear Fuel Working Group (DOE ID 2017), INL developed an action plan (INL 2017) to perform literature reviews, experimental work, and modeling to develop the technical bases for safe, extended storage of ASNF. The tasks identified are:

- Task 1 – Oxyhydroxide layer behavior and chemistry
- Task 2 – Oxide layer radiolytic gas generation resolution
- Task 3 – Sealed and vented system episodic breathing and gas generation prediction
- Task 4 – Performance of ASNF in dry storage
- Task 5 – Oxide layer response to drying

Under a Memorandum Purchase Order from INL, PNNL was requested to provide an ITR of only Task 2 and Task 3, based on expertise at PNNL in those two technical areas. The ITR provides increased defensibility of the final technical basis developed by INL and Savannah River National Laboratory (SRNL) for extended storage of ASNF.

1.3 ITR Methodology

PNNL assembled two teams of experts to perform the ITR, each team focused on one of the tasks. Given the travel and work restrictions associated with the COVID-19 pandemic, all interactions with INL and SRNL staff were via video conference, email, and phone calls and all ITR team discussions were limited to video conference.

INL provided the following documents for PNNL staff to review:

<u>Program Documents</u>

1. *Aluminum-Clad Spent Nuclear Fuel: Technical Considerations and Challenges for Extended (>50 Years) Dry Storage, Aluminum -Clad SNF Sub Working Group*, DOE/ID RPT# 1575, June 2017.
2. *Aluminum Clad Spent Nuclear Fuel Long Term Dry Storage Technical Issues Action Plan – Technical and Engineering Activities,* INL/EXT-17-43908, November 2017*.*
3. *DOE-EM Sponsored Research on Long-Term Dry Storage of Aluminum-Clad SNF,* Michael Connolly and Robert Sindelar, PowerPoint presentation to International Atomic Energy Agency Technical Meeting, March 3-6, 2020.

<u>Task 2 Specific Work Plans</u>

1. *Aluminum Clad Spent Nuclear Fuel Task 2: Oxide Layer Radiolytic Gas Generation Resolution Experiment Test Plan,* Peter Zalupski, INL/EXT-18-45858, July 2018*.*
2. *Aluminum Spent Nuclear Fuel 2020 Radiolysis Test Plan,* Christopher Verst, SRNL-RP-2020-00187, Rev. 1, June 2020.
3. *Oxide Layer Radiolytic Gas Generation Resolution: Task 2 Experimental Design,* Christopher Verst, Charles Crawford (SRNL) Elizabeth Parker-Quaife, Gregory Horne, Peter Zalupski (INL).

4. *Task 2 INL Updated Test Matrix and Updated Milestones,* INL/MIS-20-58579, Rev. 0.

Task 3 Specific Work Plans

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

Task 2 Experimental Results and Reviews

1. *Evaluation of Radiolysis Data for Hydrogen Gas Generation During Gamma Irradiation of Pre-Corroded and Pristine Aluminum Samples – An Aluminum SNF Dry Storage Study Interim Report.* Ronald Kesterson, Robert Sindelar, Christopher Verst, Gregory Horne, Elizabeth Parker-Quaife, SRNL-STI-2020-00147, Rev. 0, May 2020.
2. *Radiation-Induced Molecular Hydrogen Gas Generation by Pre-Corroded Aluminum Alloy 1100,* Elizabeth H. Parker-Quaife et al., INL/EXT-19-55202, Rev. 2, September 2019.
3. *Radiation-Induced Molecular Hydrogen Gas Generation by Pre-Corroded Aluminum Alloy 1100 – FY20 December Update,* Elizabeth H. Parker-Quaife et al.
4. *Radiation-induced molecular hydrogen gas generation in the presence of aluminum alloy 1100,* Elizabeth H. Parker-Quaife et al., Radiation Physics and Chemistry **177**:109117

Task 3 Model Reports

1. *Transient Coupled Chemical-Thermal—Fluid Field Simulation for Sealed Aluminum-clad Spent Nuclear Fuel Storage Canister,* Alexander Abboud and Hai Huang, INL/EXT-18-51683, June 30, 2018.
2. *Development of Transient Coupled Chemical-Thermal-Fluid Multiphysics Simulation for Unsealed, Vented Aluminum-clad Spent Nuclear Fuel Storage Canister,* Alexander Abboud and Hai Huang, INL/EXT-18-51681, September 30, 2018.
3. *Sensitivity Study of Coupled Chemical-CFD Simulations for Sealed and Unsealed Aluminum-clad Spent Nuclear Fuel Storage Canisters,* Alexander Abboud and Hai Huang, INL/EXT-19-52650, January 31, 2019.
4. *Full-scale Model of Dry Storage of Aluminum Clad Spent Nuclear Fuel,* Alexander Abboud and Hai Huang, INL/EXT-19-55185, Rev. 1, September 30, 2019.
5. *Guide to CFD-Chemical Model for Spent Fuel Storage*, Alexander Abboud, INL/EXT-20-58578, June 2020.

Task 4 Report for Information

1. *Aluminum Spent Fuel Performance in Dry Storage Task 4 Aluminum Oxide Sampling of ATR Dry-Stored Fuel,* Phil Winston et al., INL/EXT-58404, May 2020.

A kickoff meeting was held on June 11, 2020 via video conference with both PNNL teams and staff from INL and SRNL. The meeting was led by Josh Jarrell and Michael Connolly, the program leads. At the kickoff meeting, the following presentations were given to provide an overview of the program and individual tasks and set expectation for the ITR:

- *Extended Dry Storage of Aluminum-Clad SNF*, Josh Jarrell and Mike Connolly
- *Task 2: Radiolytic Evaluation of Molecular* Hydrogen *Generation from Aluminum Alloy Coupons,* Gregory P. Horne

- *Task 3: Modeling and Simulation of ASNF Dry Storage Environments,* Alexander Abboud.

These presentations and the accompanying discussion offered more detail and results than were in some of the published or provided documents.

Over the next two months, each team conducted three separate video conferences with staff from INL and SRNL. Each call focused on specific documents being reviewed and provided the opportunity for detailed questions and clarifications. These calls were extremely helpful in conducting the ITR. Each team used their expertise in their relevant fields in addition to further literature reviews to evaluate the data, processes, and methodologies employed by the ASNF program. The scope of the review did not include review of any raw data or the input or output files from the code runs.

Each team then drafted a report to document the areas reviewed and supply suggestions and recommendations for future work to provide assurance that the program will be successful in developing the technical bases for extended storage of ASNF. The draft reports were provided to INL for review and comment. This document addressed those comments and is the final report for the Task 2 ITR.

2.0 Outcome of Reviews

The focus of Task 2 is to determine the potential extent of gaseous hydrogen production through the radiolytic degradation of the aluminum oxyhydroxide corrosion layers present on ASNF. The radiolytic gas yield information is then provided to Task 3 to model the potential for over pressurization or flammability over the extended storage period. Given the many different fuels and aluminum alloys, variable corrosion products and thicknesses, extent of drying, etc., the program has taken the reasonable approach to develop a bounding, but not overly conservative radiolytic gas production rate to apply to all systems.

The rate of radiolytic gas production is estimated by a *G*-value, traditionally reported as the number of molecules of a compound produced or destroyed per 100 electron volts (eV) of deposited energy. More recently, *G*-values are reported in the SI units of $\mu mol\ J^{-1}$ (micro-moles per Joule), where 1 molecule/100 eV ≈ $0.1\ \mu mol\ J^{-1}$.

The Technical Issues Action Plan (INL 2017) identified one of the sub-tasks as "develop experimental test condition matrix based on temperature, in-canister atmosphere, and oxide thickness." The initial Task 2 test plan (Zalupski 2018) expanded and identified the experimental ranges for six parameters as:

1. Temperature: 25, 50, 75, 100, and 150°C
2. Atmosphere: Air, He, N_2, N_2O
3. Humidity: 0, 25, 50, 75 and 100%
4. Dose: 0, 250, 500, 750, 1000, 2000, and 3000 kGy
5. Aluminum alloy: 6061, 1100
6. Corrosion layer thickness: 1, 3, 6 µm if feasible.

The test plan (Zalupski 2018) went on to state that the aluminum specimens to be tested will take two forms: pure boehmite/gibbsite powders, and lab-grown adhered oxyhydroxide films on aluminum alloy coupons.

The Task 2 Experimental Design document (Verst *et al.*) detailed the process for testing of aluminum powders. However, the program made the decision based on literature reviews to abandon the testing of powders and focus on testing oxyhydroxide corrosion layers on aluminum. The 2020 update to the test plan (Verst 2020) showed plans to use foils, coupons, and irradiated scrap material of Al-1100.

<u>The PNNL ITR team agrees with the decision to abandon the powder testing and test the corrosion layers on aluminum coupons based on the expertise and experience of the team and associated work under the Interfacial Dynamics in Radioactive Environments and Materials (iDREAM) program sponsored by DOE.</u> The effect of the interfacial process in enhancing the H_2 generation by radiolysis, as shown by LaVerne and co-workers (e.g., LaVerne and Tandon 2002, LaVerne 2005, Reiff and LaVerne 2017), and outlined in more detail in Section 4 is of critical importance to the ASNF extended storage program. The ASNF program using corroded Al-coupons will meet the majority of the program goals, but that is dependent on how closely the coupons mimic ASNF under storage conditions.

The ASNF program's approach for determining the rate of radiolytically produced H_2 during long-term storage of ASNF involves using laboratory tests with aluminum alloy coupons in water vapor exposed to a gamma radiation field. The experiments show that H_2 generation increased for pre-corroded Al coupons demonstrating the importance of the corrosion rind as was expected based on the prior studies on the effect of Al-oxides on H_2 generation. As the temperature was raised, H_2 production increases as more boehmite (AlOOH) was produced from the alteration of the lower temperature form of Al-oxyhydroxide, bayerite (α-$Al(OH)_3$) which is a gibbsite ($Al(OH)_3$) polymorph. This was expected based on the prior work by others, notably (Westbrook *et al.* 2015). The H_2 generation rate also increased with humidity up to ~50%, and then decreased. The staff suggested that eventually the humidity is sufficiently high that the system behaves more like bulk water. These results will be discussed in greater detail in the Section 4, but were broadly expected and help show the applicability of these methods for providing data to support the long-term storage of ASNF

As discussed further in Section 4, the proposal (Verst 2020) to use scrap coupons from L-Basin for testing has the support of the ITR team especially if the scraps are of an alloy other than Al-1100 or have thicker corrosion layers.

The ITR team agrees with the conclusion in Parker-Quaife *et al.* (2019) that a focus of future work should be on radiolytic studies in a helium environment as it is anticipated that the standard DOE spent fuel canisters will be back filled with helium. The updated INL test matrix (INL 2020) outlines numerous tests to be performed under a He environment.

Finally, the ITR team agrees with the methodology and rigor outlined in the test matrices as being able to develop the *G*-values needed for the technical basis of extended storage of ASNF. However, as noted in Sections 3 and 4, there are recommendations the team feels necessary to achieve the objective of identifying a bounding, yet not overly conservative *G*-value to be used in the modeling efforts.

3.0 Optional Recommendations

1. *The ASNF program should continue to publish results in the open literature.*

The experimental approach adopted by the program yields *G*-values for input into the performance model. INL have spent significant time on the issue of scaling laboratory experiments to actual ASNF. For example, the program was concerned if the *G*-value was conservative with respect to storage conditions. INL had thoroughly discussed their approach of using the total energy deposited into the system to determine the *G*-value for H_2 production. They were challenged with this argument as it could be considered non-conservative. However, evidence of the success of their approach was the publication of this argument in the open literature (Parker-Quaife *et al.* 2020). They showed that using just the mass of the oxidized corrosion rind was overly conservative and would result in unrealistically high H_2 generation rates. The *G*-value used must be scientifically defensible as it describes the total system model for determining the safety case for the storage of ASNF. One of the best methods for developing scientific defensibility is to publish studies in the open, peer-reviewed literature. The program has succeeded in doing this.

Owing to the importance of Al-oxyhydroxides with respect to H_2 generation in a radiation environment, this review of Task 2 focused on INL's approach to investigating the interfacial processes. Many of these topics are fundamental and have been of interest to DOE-BES (i.e., the iDREAM program). iDREAM is investigating the Al-oxy-hydroxide structure and why differences in the bound water between the Al-oxy-hydroxides result in different responses to radiation fields. INL has endeavored to make use of the fundamental iDREAM studies; however, because these studies are very fundamental, it may not be completely relevant to ASNF storage environment. INL's experiments are unique and are not being performed elsewhere. The studies performed on pure Al-oxyhydroxides are of use to the INL researchers, but these other studies will not replace the important work being conducted at INL. INL understands the importance of replicating the corrosion found on the ASNF and not just concentrating on the role of the Al-oxyhydroxides. Uppermost in the research of the INL team is whether the *G*-values obtained from laboratory experiments can be scaled to the ASNF storage system. These are important questions to ask and are not being addressed by more fundamental research programs, such as iDREAM.

INL should work on additional journal publications to demonstrate that the project has been successful and obtaining peer review. INL's efforts balance the fundamental studies performed under the iDREAM program. The best method for establishing a scientific basis and consensus for ANSF storage is to publish the results from these experiments.

2. *The program should report G-values in both traditional and SI units to avoid confusion and to provide a quick check that conversions were done properly.*
3. *One or more tests should be performed at both INL and SRNL under identical conditions to understand any uncertainty or bias and provide confidence in results.*

Parker-Quaife *et al.* (2019, 2020) report that room temperature irradiations were performed at INL and high temperature (100°C, 200°C) were performed at SRNL. It is recommended to run a few similar room temperature irradiations at SRNL for direct comparison and confidence. If this has already been done, it should be made clear in reports.

4. *To provide assurance that dose rate is not a factor in determining the G-value, the test(s) suggested in #3 should be run to the same accumulated dose and compared.*

Many radiation effects, such as hardening and accumulation of damage, are sensitive to dose rate, not just accumulated dose. INL irradiations are performed with a dose rate of 46 Gy min^{-1} whereas the SRNL irradiations are performed at 18.8 Gy min^{-1} for the 200°C tests and 17.5 Gy min^{-1} for the 100°C tests. It is assumed that a room temperature test at SRNL would have a dose rate less than that at INL, but if both tests reach the same accumulated dose, a comparison of the results will show if dose rate is important. Given the wide range in the age of the ASNF to be stored, dose rates would be expected to be quite variable from canister to canister.

5. *The ASNF program should avoid stating that an objective of the program is to study or develop mechanistic explanations of radiolytic gas generation (Zalupski 2018)*

To probe mechanisms, there should be additional controls in the experiments combined with molecular modeling. For example, Shen *et al.* (2017) performed density functional theory (DFT) calculations on the energetics of radiolytic species across the interface between different crystal planes of AlOOH. These calculations showed that the release of $H^{\bullet}$ from boehmite into the solution was exothermic; whereas the $O^{\bullet}$ remained trapped at the surface. It is this type of work that can lead to understanding the mechanisms of H_2 release but may not be applicable or necessary to the determination of an input *G*-value for predicting H_2 concentrations in an ASNF storage canister. The program should call their studies applied science investigations relevant to ANSF storage, not mechanistic studies.

4.0 Key Recommendations

The recommendations in this section are considered critical and necessary to show with confidence that the *G*-values determined are bounding but not overly conservative, and scalable to the canister level.

1. *The program should perform at least some scoping tests on Al-6061 under the same conditions as Al-1100. If significant differences in H_2 generation are observed, the alloy with a more bounding G-value should be the focus of continued testing.*

The initial test plan by Zalupski (2018) identified testing both Al-6061, which has ~1.0% magnesium and ~0.6% silicon, and Al-1100 which is commercially pure aluminum. Al-6061 is the alloy used for fuel for ATR, HFIR and the University of Missouri Research Reactor (MURR) and is therefore the most predominant alloy in the inventory. Results published to date have only looked at Al-1100. Similarly, the updated test plans (Verst 2020 and INL 2020) both continue to only look at Al-1100. In Section 2.1 of Verst (2020), it is assumed that “differences in alloy composition are considered not significant factors in radiolytic gas production from hydrated oxides-on-aluminum substrates.” The PNNL ITR team does not agree that there is sufficient basis for this assumption.

SRNL analyzed surfaces of ASNF canisters with a scanning electron microscope (SEM) from several different types, including; Uruguay reactor element (RU-1) (Al-1100), MURR-(Al-6061), SRS Universal Sleeve Housing (AA-6063), and SRS Mark-16b production reactor (AA-6061 and AA 6063) (see Table 1) (Connolly and Sindelar 2020). The results from this study are difficult to explain because, in the case of the AA-1100 alloy exposed to in-reactor conditions for 8 years, only produced gibbsite ($Al(OH)_3$) on the surface; whereas, AA-6061 generated boehmite (AlOOH) in 0.3 years in-reactor exposure. The wet storage temperature was 22°C which would be unlikely to result in the formation of boehmite but might result in other changes to the surface.

Table 1. Characterization of Stored ASNF (Connolly and Sindelar 2020)

Al-cladding	In-reactor (yrs)	Storage (yrs)	Comments
AA-1100	8	30 (dry)	gibbsite 200 nm to 25 µm
AA-6061	~0.3	<18 (wet)	bayerite and boehmite 5 to 10 µm
AA-6063	~5	~40 (wet)	boehmite and bayerite – dense film

These results on the phase distributions shown in Table 1 may indicate that the characterization was incomplete or regions which were somehow protected when examined. Each alloy also contains impurities within the metal. These are typically Fe, Mg, and Si. Figure 1 is an SEM elemental map of an Al-clad U-Mo fuel showing these impurities in the metal. There was no information on the fate of these impurities in the SRNL study despite evidence that suggested the effect of impurities on the corrosion rind was visually obvious. INL has also conducted PIE investigations of the aluminum alloy cladding; however, these investigations need to be better integrated into the INL H_2 generation study. The role of the impurities in H_2 generation needs to be determined.

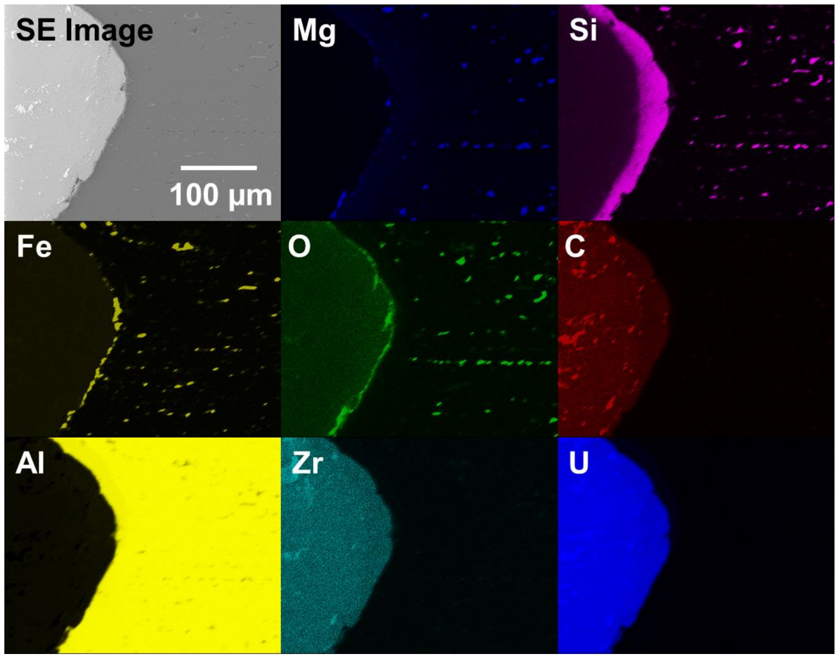

Figure 1. The AA6000 series cladding contains many different impurity elements that may impact the production of H_2 gas.

If the impurities are important to the radiolytic behavior, then there could be differences between the different alloys. Some additional coupon testing with different AA-series materials with a close attention to the phase distribution and the role of impurities is needed.

Experience from Hanford waste tanks and synthesis studies show that high temperatures are needed to form boehmite, otherwise gibbsite or bayerite dominates (Chatterjee *et al.* 2016).

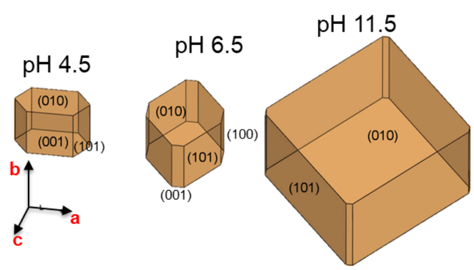

Figure 2. Schematic of the changes in boehmite morphology with pH. (Chiche *et al.* 2011)

Boehmite is orthorhombic (**a** = 0.0285 nm, **b** = 0.1224 nm and **c** = 0.0365 nm). The crystals are typically tabular with the major surfaces normal to **B**[010]; however, the morphology can change dramatically depending on the formation conditions (see Figure 2). In Figure 3, SEM images of boehmite formed under different conditions are shown. It may be important when trying to model H_2 generation rates from ASNF, that the nature of boehmite and/or bayerite formation is understood. At Hanford, the formation of boehmite occurred during temperature excursions from excessive amounts of Cs137 and Sr90 that caused precipitated gibbsite to transform to boehmite (Peterson et al. 2018). Both INL and SRNL reported identification of bayerite rather gibbsite. These are structurally very similar although the differences can be readily revealed with X-ray diffraction (XRD). Do these differences result in any changes in water content and possible release of H_2 gas during irradiation? The iDREAM program and others investigating these effects have reported results for gibbsite not bayerite. It is not clear if the SRNL studies imply formation of boehmite at relatively low temperatures during wet storage of ASNF. Could a radiation field in combination with long-term underwater storage result in boehmite formation? If so, this should be explored more closely as this process could have a large impact on the subsequent H_2 generation from radiolysis during storage.

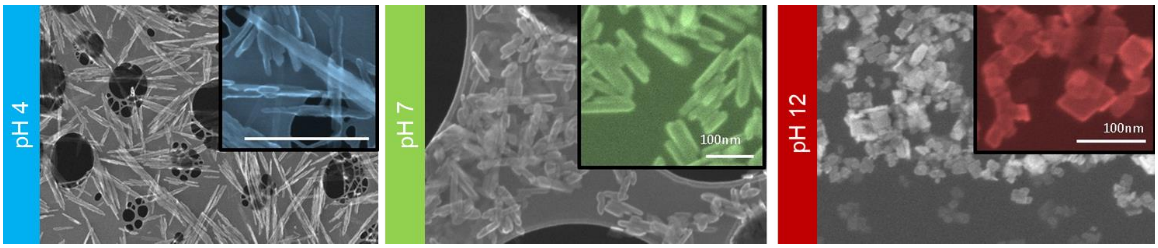

Figure 3. SEM images of boehmite formed at different pH conditions. (taken from Conroy et al. 2017)

2. *A more concentrated effort to link the tested specimens to the actual ASNF cladding and corrosion products should be made. Specifically, the effect of increased corrosion layer thickness and of larger scales should be investigated.*

The initial test plan (Zalupski 2018) and the reported results (Parker-Quaife *et al.* 2019) show that testing has been performed on pre-corroded Al-1100 with on oxide film thickness of ~5 µm. Table 1 shows that actual stored ASNF can have significantly larger thickness, up to 25 µm for Al-1100. The effect of this increased thickness, with both more water and absorbing more of the dose, on H_2 production needs to be known to be assured that the calculated G values are bounding for the realistic systems.

The *G*-values reported by Parker-Quaife *et al.* (2019) were all ≤ 0.0093 (0.00096 µmol/J) at ambient temperature, which are far lower than bulk water [0.46 (0.048 µmol/J)]. The *G*-values reported by several groups on metal oxides (as described earlier), show much higher values, including for pure boehmite powders. However, an important distinction was made by the INL group on this point. The total system in the experiments includes the gas environment, the gas-liquid boundary, the sorbed liquid, the oxide, and the metal. The same is the case for the storage system. Energy from radiation is deposited into all these regions proportional to the electron density of the components, meaning that most energy must be deposited into the metal (i.e., cladding). INL stated that it would be difficult to calculate the various charge transfer mechanisms, the $G_\gamma(H_2)$ values from the laboratory experiments were reported with respect to the dominating material, the metal. Is this a non-conservative approach if scaled to the ASNF canister?

The impact of the Al metal on attenuating most of the radiation dose (and hence lowering G_{eff} for H_2 production) can be seen in the XRD results of the corroded coupons. The X-ray beam also mainly interacts with the dominant metal which made it difficult to determine the nature of the corrosion rind in the INL experiments. The XRD analysis in the INL work demonstrates why the total dose to the system should be used instead of trying to calculate H_2 generation based only on the dose to the corrosion rind.

This example of the XRD analysis shows why it is scientifically defensible to use the entire system. The inputs to the PA model for H_2 production include the radiation dose over time in the ASNF storage environment and the *G*-value. The *G*-value is obtained from experiments on corroded Al-coupons. If a significant amount of the radiation is absorbed by the bulk metal, then the calculated *G*-value will reflect the actual production rate for H_2 in the storage system. However, if the coupons are not good representations of the corroded ASNF material, this assumption will breakdown.

The *G*-values calculated by the LaVerne group and others during these interfacial experiments are high relative to bulk water. This occurred because the investigators calculated the dose that the oxide must have received based on energy deposition calculations. In the program experiments, it is the thin-layer of corrosion rind that controls H_2 production but the dose in the storage environment is absorbed mainly by the dominant Al-metal. If the *G*-value was based only on the dose delivered to the corrosion rind and contacting water, it would result in excessively high *G*-values. The choice to use the entire irradiated system and not just the corrosion rind, is a scientifically defensible approach; however, it does depend on whether the coupons correctly mimic the ANSF canisters correctly. If so, this approach can be scaled to the ASNF storage system.

The objective of this study was to generate a *G*-value that can be used in the models. It is important not to be overly conservative and to not under-estimate the H_2 generation. The researchers accounted all interfacial regions in the calculation of the *G*-value. As much of the radiation energy is lost to the metal and does not result in radiolysis, by including this quantity in the calculation, the effective *G*-value was lowered. This is the correct and scientifically defensible methodology. However, it does require that any disparities between the coupon experiments and the actual ASNF be known. If there is too little corrosion in the laboratory experiments compared to the ANSF fuel, then the *G*-value will be underestimated.

3. *More detailed surface characterization, specifically the surface area of the corrosion rind on the specimens before and after irradiation is needed.*

To understand the increase in H_2 production for the heterogeneous system relative to bulk water, it is critical that the Al-oxyhydroxides produced on the coupons are thoroughly characterized, including the potential role of possible minor components/phases in the alloys. The program is using the tools available to conduct these types of examinations, but additional characterization would help their investigations. The program has compared their characterization results with actual post-irradiation analysis of stored ASNF as much as possible. Accurate information on the surface area generated under specific conditions (as H_2 production rate is a function of surface area), composition (because changes in composition and oxidation state will control H_2 formation from the surface), and phase distribution (because different phases generate different amounts of H_2) is needed.

It may be possible to determine the phase using Electron Backscattered Diffraction (EBSD) analysis of polished cross-sections to match with XRD analysis. If there are variable phases, then EBSD may be more useful than XRD which will only provide a bulk analysis but not the distribution of the phases and is overwhelmed by the signal from the Al-metal. The location of the specific phases could be important with respect to understanding their role in H_2 generation. It is also possible that many of the phases produced will be X-ray amorphous and might not yield good quality EBSD signals, in which case, it might be advisable to obtain Transmission Electron Microscopy (TEM) samples of the layer. Infrared and Raman are also effective methods for analyzing the corrosion rinds. Reiff and LaVerne (2017) used X-ray photoelectron spectroscopy (XPS) to determine the oxidation state of Al on a surface and will indicate how H_2 is being released. It is important to quantify the surface are of the corrosion ring so that the impact of the surface with environmental changes is known.

Atomic force microscopy (AFM) could also be used to examine the corroded surface. Examples of using this method in-situ with a radiation field operating have been demonstrated by the iDREAM program. It is clear from the work of others in this field, that the specific crystal planes and the proportion of these also impact radiolytic yield. TEM can provide information on the formation of phases such as boehmite that may be too small for SEM and XRD.

4. *Scoping studies of irradiations at temperatures of ~165°C and ~175°C should be performed to better understand the significant (3-4-fold) increase in H_2 generation observed at 200°C.*

Bayerite is known to transform to boehmite at temperatures around 170°C. Since boehmite exhibits a higher rate of H_2 production relative to bayerite (Parker-Quaife *et al.* 2020), this could explain the 3-4-fold increase observed. If this transition is the cause of the increased H_2 production, that will be very important in determining drying and storage conditions. By performing tests at relatively close temperatures that bracket the transition temperature, it may be possible to determine if bayerite transition is important.

The oxyhydroxide pre-filming processes proposed in Section 3.1.1 of Verst (2020) should also be performed. Some coupons will have approximately 7 µm of predominantly boehmite and others will have approximately 8 µm of bayerite/gibbsite and be tested under similar conditions.

The use of variable (i.e., increasing) oxyhydroxide thicknesses will also help determine if the increase in H_2 generation at higher temperatures is associated with “annealing” or more efficient release of H_2 trapped in the oxide film.

5.0 Conclusions

PNNL staff performed an ITR of the ASNF program Task 2. The objective of Task 2 is to determine *G*-values for the radiolytic production of gaseous molecular hydrogen from the aluminum oxyhydroxide layers present on ASNF cladding. The *G*-values need to be defensible, bounding, but not overly conservative. As part of the ITR, the team reviewed program documents, Task 2 work plans, and results to date. In addition, the team held three separate video conferences with the program research staff to ask clarifying questions and obtain additional detail. The PNNL ITR team concludes that if the program follows the methodology and rigor outlined in the test matrices, the program will develop *G*-values for a defensible technical basis of extended storage of ASNF.

Specifically, the ITR team:

- Agrees that testing of corrosion layers on aluminum coupons is appropriate and testing of powders is not needed.
- Agrees that future work should focus on radiolytic studies in a helium environment, as it is anticipated that the standard DOE spent fuel canisters will be back filled with helium.
- Supports the proposal to test scrap coupons from L-Basis, especially if the scraps are an alloy other than Al-1100 or have corrosion layers thicker than 5 µm.

The ITR team has the following recommendations that would increase confidence in the test results and overall program:

1. The ASNF program should continue to publish results in the open literature.
2. The program should report *G*-values in both traditional and SI units to avoid confusion and to provide a quick check that conversions were done properly.
3. One or more tests should be performed at both INL and SRNL under identical conditions to understand any uncertainty or bias and provide confidence in results.
4. To provide assurance that dose rate is not a factor in determining the G value, the test(s) suggested in #3 should be run to the same accumulated dose and compared.
5. The ASNF program should avoid stating that an objective of the program is to study or develop mechanistic explanations of radiolytic gas generation.

The ITR team determines that the following recommendations are critical and necessary to meet the program objective with confidence and defensibility:

6. The program should perform at least some scoping tests on Al-6061 under the same conditions as Al-1100. If significant differences in H_2 generation are observed, the alloy with a more bounding G value should be the focus of continued testing.
7. A more concentrated effort to link the tested specimens to the actual ASNF cladding and corrosion products should be made. Specifically, the effect of increased corrosion layer thickness and of larger scales should be investigated.
8. More detailed surface characterization, specifically the surface area of the corrosion rind of the specimens before and after irradiation is needed.
9. Scoping studies of irradiations at temperatures of ~165°C and ~175°C should be performed to better understand the significant (3-4-fold) increase in H_2 generation observed at 200°C.

Following these recommendations, most of which are part of the original test matrix proposed by Zalupski (2018), will enable the well-qualified research team to reach the program objective and provide a defensible technical basis for extended storage of ASNF.

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