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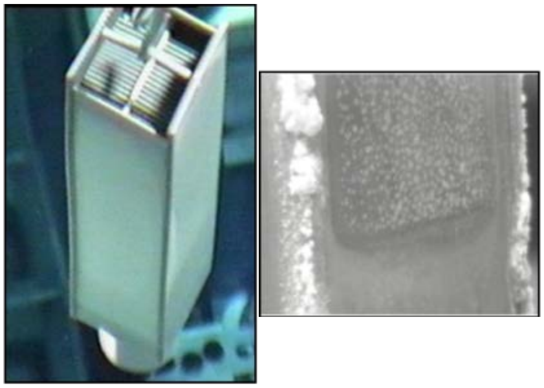
Oxyhydroxides on Aluminum Spent Nuclear Fuel: Formation Studies and Removal Practices to Prevent Radiolytic Gas Production



(Left) Aluminum-clad fuel assembly with intact, protective oxyhydroxide film after long-term wet storage in good-quality water; (right) trihydroxide deposits due additional corrosion during wet storage in poor water quality (SRNL photographs)

Aluminum-clad nuclear fuel has been at the forefront in research and commercial reactors. After being removed from the reactor, the spent nuclear fuel is placed in large-volume water basins (wet storage) that are constantly monitored for water quality to minimize corrosion/deterioration. The water provides both radiation shielding and cooling for the freshly removed fuel. It is highly desired to have a pathway for fuel to be transitioned to dry storage in sealed casks, so that spent nuclear fuel can be safely transported and dispositioned in a permanent repository, and basin capacity can be made available for temporary wet storage of fresher spent fuel. A challenge for safe, road-ready dry storage is the hydrated aluminum oxides (oxyhydroxides) that are prevalent on aluminum spent nuclear fuel that has been stored under water for years. If water is released from the oxyhydroxides during dry storage, it can create corrosion within the storage canister, and hydrogen can be generated through radiolysis of the oxyhydroxides, causing pressurization and flammability risks. The focus of this project is to develop knowledge of the oxyhydroxide growth and production of gases through radiolysis and to apply empirical models for predicting these phenomena. The expertise developed will be used to formulate conditions and parameters for oxyhydroxide removal/dehydration from fuel cladding through vacuum or forced-air gas drying, to prevent problems during permanent dry storage.

Awards and Recognition

As part of this LDRD effort, SRNL was awarded an Environmental Management Technology Development Award (EM-TD) of $ 1.66 million for FY18 and FY19. Additionally, funding that was supplied to the University of South Carolina has provided us resources and expertise for drying technologies currently in research and development for commercial nuclear fuel.

Intellectual Property Review

This report has been reviewed by SRNL Legal Counsel for intellectual property considerations and is approved to be publically published in its current form.

SRNL Legal Signature

Signature

Date

LDRD-2018-00032
LDRD Report

Oxyhydroxides on Aluminum Spent Nuclear Fuel: Formation Studies and Removal Practices to Prevent Radiolytic Gas Production

Project Team: R. E. Fuentes (co-PI), A. L. d'Entremont (co-PI), C. Verst, C. Crawford, L. C. Olson, B. L. García-Díaz, K. Metzger and R. L. Sindelar

Subcontractor: T. Knight and M. Shalloo, University of South Carolina

Thrust Area: NMM

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Aluminum-clad Spent Nuclear Fuel (ASNF) has chemically-bound water in the form of hydrated oxides or hydroxides (oxyhydroxides) on the cladding surface due to water exposure during irradiation and storage. This presents a challenge to sealed (road-ready) dry storage. To assess the risks associated with oxyhydroxides on ASNF for dry storage, it is necessary to understand their growth/formation and morphology as the precursor state for drying and their gas generation from radiolysis. This will help determine safe oxyhydroxide loadings on dry-stored fuel as well as methods of removal. In this work, oxyhydroxides were grown on aluminum substrates and the resulting layers were studied for morphology and thickness. Radiolysis studies were performed on powders to establish a correlation between morphology and particle size on gas generated. These experiments, along with literature data, will be used to develop models and drying methods for use in establishing safe dry storage conditions.

FY2018 Objectives

- Integrate literature models for oxyhydroxide formation and growth into a composite model and perform heat flux immersion experiments for oxyhydroxide formation to validate the model.
- Establish irradiation and gas sampling apparatus with test protocols for a range of material system and irradiation conditions and measure radiolytic gas generated from materials.
- Investigate thermal treatments and parameters to determine conditions required for adsorbed water removal and chemically-bound water removal.

Introduction

Safe storage with end-state disposition of Aluminum-clad Spent Nuclear Fuel (ASNF) is a major mission for Nuclear Material Management Programs (NMMP), with National Nuclear Safety Administration (NNSA), Department of Energy – Office of Environmental Management (DOE-EM) and Office of Science (DOE-SC), and Commerce Department customers. Water chemically-bound in the form of hydrated oxides or oxyhydroxides on aluminum cladding is prevalent on ASNF. This presents a challenge to sealed (road-ready) storage because oxyhydroxides can decompose and generate gases (e.g., oxygen, hydrogen) due to radiolysis that may cause pressurization, flammability conditions and corrosion within the storage container. The technical and engineering gaps that need to be addressed for safe storage and transportation were compiled in a recent report[1].

The formation and growth of oxyhydroxides on aluminum is dependent on temperature, heat flux and water quality; the formation and growth can occur both in reactor and while the ASNF is in wet storage in water basins for an extended period. A single model to predict the cumulative growth of oxyhydroxide from in-reactor use through long-term pool and dry storage is lacking in the literature. This LDRD was established to (1) investigate a unified model to predict oxyhydroxide formation on ASNF using thorough literature research and experimental results, (2) investigate radiolytic gas production dependence on oxyhydroxide form (e.g., gibbsite, bayerite, boehmite) by developing an irradiator and gas sampling apparatus, and (3) establish thermal processes for removal of oxyhydroxide films/layers. Experimentally grown oxyhydroxide layers will be characterized for morphology, thickness and surface conditions to facilitate both the modeling and drying efforts.

During FY18, oxyhydroxides were grown on Al substrates using hot wall tests. The resulting layers were characterized using X-ray Diffraction (XRD) to evaluate the resulting composition/chemical structure (e.g., gibbsite, bayerite, boehmite) and using Scanning Electron Microscopy (SEM) to examine surface morphologies and measure layer thickness. Improved understanding of surface structure coupled with literature review will help us to develop a composite model (currently in progress). Radiolysis and simultaneous thermal analysis (STA) was performed on oxyhydroxide powders with known composition and defined particle size to determine the dependence of hydrogen generation on oxyhydroxide type and morphology/particle size and to identify parameters and temperatures for the removal of residual water. The work encompasses routes for growth, radiolysis and drying to advance the understanding of the aluminum oxyhydroxides on ASNF to estimate the layers that exist on actual fuel and to establish processes for removal prior to (extended) dry storage with ultimate permanent disposal in a repository.

Approach

Oxyhydroxides were grown on aluminum substrates primarily using a hot-wall immersion method in the experimental setup shown in Figure 1. This setup heats the water bath through the aluminum sample, providing a heat flux across the surface exposed to water. This is suitable for replicating conditions in which heat flows in a prescribed direction (e.g., heat transferred to Al fuel cladding in reactor as well as during spent fuel pool storage due to attendant decay heat). Growth tests spanned a temperature range from 25°C to 100°C at times to evaluate growth kinetics. Characterizations including XRD and SEM were used to analyze the resulting oxyhydroxide.

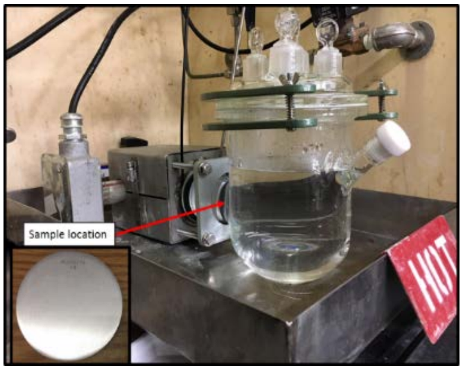

Figure 1. Hot-wall setup showing the location of the Al alloy disc specimen.

Figure 2. Gas collection tool for radiolytic gas generation tests. The inset picture shows a glass ampoule pf oxyhydroxide powder before (left) and after (right) irradiation.

Radiolytic gas generation from oxyhydroxides was measured using oxyhydroxide powder. Glass ampoules to hold the powder were made in the glass shop and were vacuum purged, helium filled, and flame sealed. The ampoules were placed in the SRNL Co-60 irradiator for a given time and the gas generated was removed using a purged collection tool by sealing the sample inside and cracking the glass to release the gas. The gas was analyzed using gas chromatography (GC). A picture of the collection tool is shown in Figure 2 with an inset showing a flame-sealed glass ampoule containing powder before and after irradiation. STA of oxyhydroxide powders was also used to understand morphology transition and establish parameters for drying.

Results/Discussion

Hot wall immersion was used to grow oxyhydroxide films on specimens of three different aluminum alloys at various temperatures and durations. For example, Figure 3 shows SEM images of the surface of Al 1100 after 100°C hot-wall exposure for 7 days (left) and 41 days (right). XRD analysis indicated that the film was predominantly boehmite with no evidence of trihydroxides. For 100°C, either pseudoboehmite or crystalline boehmite is the expected phase[2]. SEM images of the surface morphology (Figure 3) showed a predominantly "needle-like" appearance of the oxide structure, which appears to correspond to platelets roughly perpendicular to the substrate and with random rotation, so that the edges of the platelets are seen from this angle. This morphology is consistent with oxyhydroxide morphologies described in the literature after immersion in 100°C water (studies were short-term, up to 2 h)[3,4]. There are also scattered "scale-like" features (Figure 3, right) that appear to be overlaid over the "needle-like" morphology after longer-duration exposure (41 days). Cross-section of the samples showed a total film thickness ranging from about 0.5 to 2 µm with appearance of a single-layer film. In parallel, a literature review was conducted to identify existing models and data for oxyhydroxide growth, to determine what environmental conditions have been observed to significantly impact the growth, and to gain insight into the physical mechanisms involved.

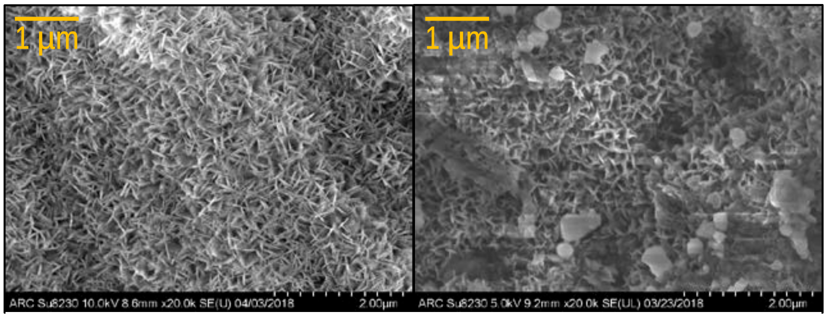

Figure 3. SEM images of Aluminum 1100 in hot-wall test at 100°C for 7 days (left) and 41 days (right).

Radiolysis tests were performed on oxyhydroxide powders to measure the radiolytic gas yield and the impact of grain size and adherence and provide gas generation differentiation depending on oxyhydroxide morphology. The powders used consisted of gibbsite with particle size ~15 µm, coarse boehmite with particle size ~77 µm and fine boehmite with particle size ~0.7 µm and were used as a first step prior to use of specimens with oxide films developed on aluminum coupon substrates. Measured G values were compared with literature data to validate of the experimental setup. The powders, contained in glass ampoules, were irradiated, and the concentration of released hydrogen was measured to compute G values. Table 1 shows the hydrogen concentrations obtained for each powder in ppm and the calculated hydrogen G values, along with corresponding literature G values. As listed in the table, the boehmite powders yielded significantly more radiolytically produced hydrogen than the gibbsite powder: over two times more for the fine particle size and over seven times more for the coarse particle size. This is consistent with previous studies that found greater radiolytic hydrogen production for boehmite than for gibbsite[5]. While the initial powder results do fall in line with literature trends and ranges, the current results do not represent a statistically significant sample size.

Table 1. Hydrogen concentration and hydrogen G-values obtained from three powders.

Sample	Sample Dose (Rad)	H_2 Concentration (ppm)	H_2 G Value (mols/J x 10^{-7})	Derived G Values from literature[6] (mols/J x 10^{-7})
Gibbsite	16.67	502	0.0331	0.021
Boehmite (coarse)	16.67	3612	0.1911	0.057 - 0.13
Boehmite (fine)	16.67	1337	0.0783	

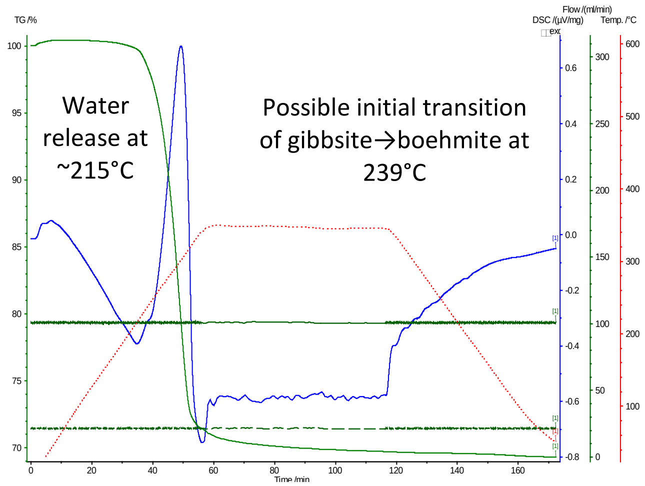

Figure 4. STA results using gibbsite powder.

STA tests combining Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) were performed on oxyhydroxide powders to explore their dehydration behavior. Figure 4 shows results for gibbsite powder. The sample was heated to 350°C at a rate of 5°C/min and held for 1 hour, followed by cooling at the same rate down to 20°C. The points of importance are where the DSC curve turns sharply upward and when the TG curve begins to turn downward. These represent changes in energy transfer and the remaining percentage of starting mass, respectively. The most notable event is at 215°C where the DSC's upward turn (blue line) corresponds directly to the TG's downward turn (green line) indicating water evaporation. The total mass loss was approximately 30%. There was also a small change in slope of the DSC curve at about 239°C which could be indicative of an initial phase change to boehmite. A small vacuum chamber for drying tests has been constructed at the University of South Carolina (USC) for oxyhydroxide removal. Figure 5 shows a schematic diagram of the chamber and a picture of the inside showing the two heater rods. The chamber will be used for oxyhydroxides grown on Al substrates using parameters and conditions determined from the STA analysis.

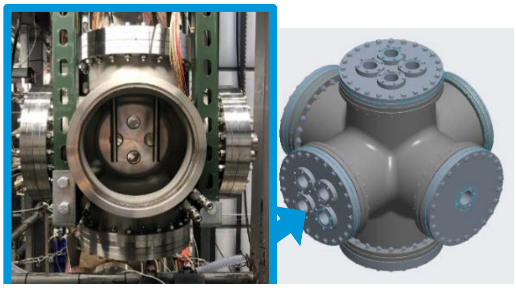

Figure 5. Vacuum gas chamber schematic with a picture of the inside of chamber showing two heater rods.

FY2018 Accomplishments

- The growth of oxyhydroxide layers and their response to irradiation and drying strategies is being investigated to facilitate long-term, sealed dry storage of Al-clad spent nuclear fuel.
- Literature review on Al aqueous corrosion has been conducted to guide experimental efforts and develop a predictive model for oxide content on ASNF.
- Oxyhydroxide films have been successfully grown and characterized using a "hot-wall" setup designed to simulate heat flux through fuel cladding, for several Al alloys at different temperatures.
    - Improves understanding of oxide growth under well-controlled conditions
    - Non-radioactive specimens for drying and/or radiolysis tests
- A radiolysis test apparatus has been established and used to obtain G-values for H_2 release from oxyhydroxides. This capability has been successfully demonstrated on powders.
- A drying chamber has been constructed at USC and is expected to perform testing on lab-grown oxyhydroxides in FY 2019.

Future Directions

- Refine modeling using additional experimental results.

- Validate model with information from L-basin fuel of known power history and storage conditions and/or coupons with prescribed thermal profile for typical oxyhydroxide formation.
- Continue growing oxyhydroxides under varying well-controlled temperature and water conditions. Leverage knowledge from previous experiments and literature to accelerate growth of thicker and/or denser films.
- Investigate thermal treatments to determine temperatures required for water removal (i.e., physiosorbed and chemisorbed) using vacuum drying chamber at University of South Carolina.
- Explore drying technologies for ASNF using heated gas and forced gas dehydration with drying chamber and with scaled-up demonstration.

FY 2017 Publications/Presentations

None

References

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Acronyms

ASNF	Aluminum Spent Nuclear Fuel
DOE-EM	Department of Energy - Office of Environmental Management
DOE-SC	Department of Energy - Office of Science
DSC	Differential Scanning Calorimetry
GC	Gas Chromatography
NMMP	Nuclear Materials Management Programs
NNSA	National Nuclear Security Administration
SEM	Scanning Electron Microscopy
STA	Simultaneous Thermal Analyzer
TGA	Thermogravimetric Analysis
XRD	X-ray Diffraction

Intellectual Property

None

Total Number of Post-Doctoral Researchers

None