Contract No:

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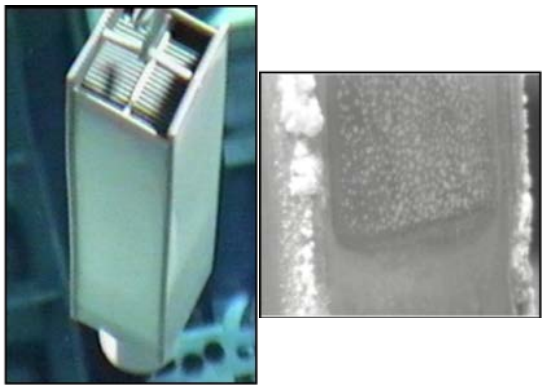
Disclaimer:

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 Spent Nuclear Fuel (ASNF) forms hydrated oxides or (oxy)hydroxides on the cladding due to water exposure during irradiation and storage. For dry storage in sealed casks, (oxy)hydroxides can pose challenges due to risks of release of bound water and decomposition releasing hydrogen and/or oxygen. To assess these risks, growth/formation of (oxy)hydroxides films on aluminum alloys, used in ASNF cladding, was investigated as the precursor state for drying. In addition radiolytic gas generation (of H_2 and O_2) of (oxy)hydroxide powders was measured and thermal drying tests were performed on both powders and adherent (oxy)hydroxide films on coupons. This research will help to determine safe (oxy)hydroxide loadings on dry-stored fuel as well as methods of removal.

Thick (>5 micron), blocky bayerite films resembling those on sampled ASNF materials were grown via aqueous corrosion of aluminum alloy coupons and used in the drying tests. Drying tests were performed using thermogravimetric analysis (TGA) and differential scanning calorimetry on gibbsite and boehmite powders to identify key temperature ranges/thresholds for the thermal decomposition reactions and impacts of ramp rate and hold times for drying of isolated, high-surface-area (oxy)hydroxides. The results were used to inform drying of adherent (oxy)hydroxide films. TGA drying tests of small Al alloy coupons with adherent (oxy)hydroxide films were performed in conjunction with pre- and post-drying characterization. Results suggest that significant drying occurs within a key temperature window of ~200-250˚C, and reveal that contraction of the film drying produces severe cracking and spalling of the oxide.

Awards and Recognition

As part of this LDRD effort, SRNL was awarded an Environmental Management Technology Development Award (EM-TD) of $ 2.5 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

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Signature	**Date**

LDRD-2018-00032
LDRD Report

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

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

Thrust Area: NMM

Project Start Date: October 1, 2017
Project End Date: September 30, 2019

Aluminum-clad Spent Nuclear Fuel (ASNF) forms hydrated oxides or (oxy)hydroxides on the cladding due to water exposure during irradiation and storage. This poses challenges to sealed (road-ready) dry storage due to risks of release of bound water and decomposition releasing hydrogen and/or oxygens. To assess the risks, it is necessary to understand the (oxy)hydroxides' growth/formation and morphology as the precursor state for drying and their gas generation from radiolysis. This will help determine safe (oxy)hydroxide loadings on dry-stored fuel as well as methods of removal. In this work, (oxy)hydroxides were grown on aluminum alloy substrates and the resulting layers studied for morphology and thickness; radiolysis studies were performed on powders to correlate morphology and particle size to gas generation, and drying studies were performed on powders and adherent oxide films. These experiments will be used to guide development of drying strategies for safe dry storage.

FY2019 Objectives

The radiolysis testing of (oxy)hydroxide powders was completed in FY18, so FY19 focused on continued investigation of (oxy)hydroxide growth and on the drying tests.

- Grow thick and/or dense (oxy)hydroxide film surrogates more characteristic of those on actual ASNF for use in dehydration testing.
- Investigate thermal treatments to determine temperatures require for adsorbed water removal.
    - Perform thermal drying tests on (oxy)hydroxide powders to determine time and temperature requirements.
    - Perform thermal drying tests on adherent (oxy)hydroxide films on aluminum

Introduction

The aluminum cladding of research-reactor fuel undergoes general corrosion with resulting formation of adherent aluminum (oxy)hydroxide films during in-reactor and post-discharge exposure to water. These films have different crystalline structures and morphologies due to various conditions and temperatures while immersed in water. For extended dry storage of ASNF, (oxy)hydroxides poses challenges due to the risk of thermal or radiolytic decomposition releasing water and/or hydrogen and oxygen gases. For this study,laboratory experiments investigating formation of (oxy)hydroxides under exposure to water at various temperatures and durations were conducted. In addition, radiolytic yield of hydrogen from aluminum (oxy)hydroxide powders and thermal drying behavior of aluminum (oxy)hydroxides (in both powder and adherent film forms) were measured to identify approaches for reducing bound water on fuel cladding prior to sealed dry storage. Effective drying strategies for adherent (oxy)hydroxides on fuel cladding will improve the safety of dry storage by mitigating potential avenues for additional corrosion and/or generation of flammable gases inside the storage canister.

Approach

The work this year continued to investigate aqueous corrosion of aluminum coupons to grow adherent (oxy)hydroxide films as surrogate oxides for drying tests, with an aim to obtain thicker and/or denser films. Changes from earlier testing included extended exposure durations (up to 16 weeks), a wider temperature range (down to room temperature for producing trihydroxides and up to 185°C, under pressure, for producing boehmite), and increased use of isothermal immersion tests after confirming no apparent differences between films formed under a heat flux versus those under isothermal conditions. Coupons were sanded with 600 grit on the target face for oxide growth in order to remove existing oxides that might impede formation of the (oxy)hydroxide.

Experiments were also conducted to investigate thermal dehydration of aluminum trihydroxides (bayerite and gibbsite) characteristic of low-temperature (< 80°C) corrosion in water and aluminum oxyhydroxide (boehmite) characteristic of high-temperature (> 80°C) corrosion in water. First, commercially produced (oxy)hydroxide powders (boehmite and gibbsite) were tested via thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The effort aimed to identify or confirm key temperature ranges/thresholds for the thermal decomposition reactions, as well as impacts of ramp rate and hold times, for drying of isolated, high-surface-area (oxy)hydroxides. Powder tests were conducted up to 1000°C to ensure capturing complete dehydration to alumina, and some tests were conducted with temperature holds of various temperatures and durations with the aim of isolating different phases of the drying behavior. The information gleaned from powder tests was used to guide subsequent drying tests on adherent (oxy)hydroxide films grown on aluminum alloy substrates. TGA was used to analyze small samples of the aluminum coupons with adherent (oxy)hydroxide films. The samples were tested at drying temperatures of 200, 220, 260, and 500°C and were held at the test temperature for long durations with the aim to determine the maximum dehydration achievable at that temperature. Specimens were characterized both pre- and post-drying using X-ray diffraction (XRD) to determine the film composition and scanning electron microscopy (SEM) to determine its morphology in both planview and cross-section.

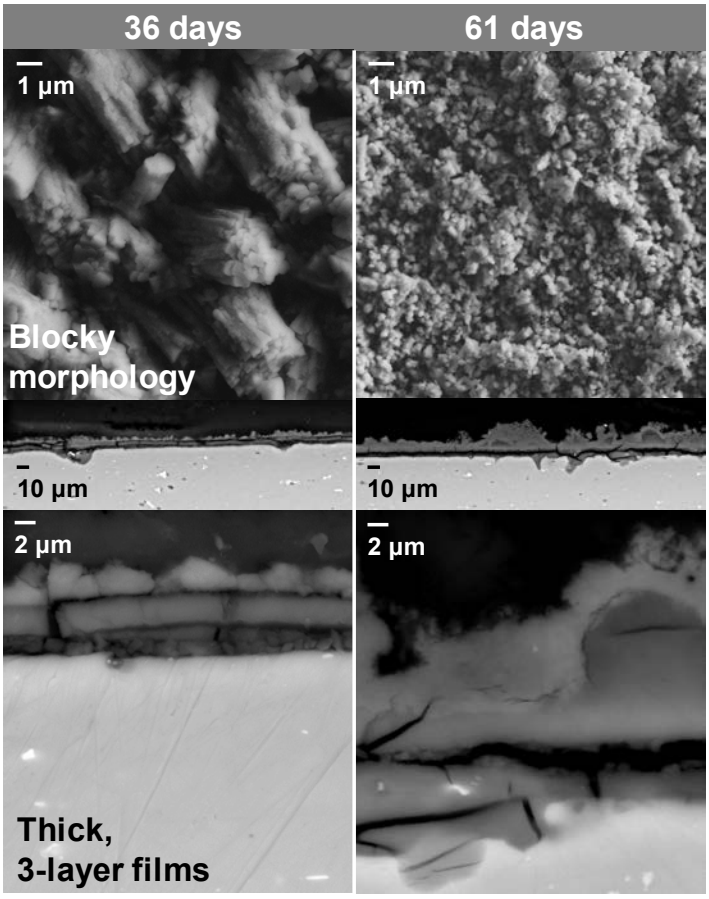

Figure 1. Hydroxide films formed by aqueous corrosion in room-temperature water for (left) 36 days and (right) 61 days. (Top) planview SEM, (middle and bottom) cross-section SEM.

Results/Discussion

Thick, blocky bayerite films (Figure 1) were found to form relatively rapidly on coupons in room-temperature water, more so than in 50°C water. This was unexpected, as corrosion kinetics were expected to be accelerated by increasing water temperature. Literature sources [1] indicate that pseudoboehmite is the first phase to develop during formation of Al (oxy)hydroxides in water, and the transition point between formation of trihydroxides and boehmite is known to be near 80°C, so it is hypothesized that the development of pseudoboehmite into the trihydroxide may occur more rapidly at temperatures further from this transition temperature. Exposure to room-temperature water for 36, 38, and 61 days produced three-layered films averaging about 8, 11, and 20 µm thick, respectively. XRD indicated that these films consisted predominantly of bayerite with some boehmite. The films produced roughly resemble those found on sampled ASNF materials stored wet in L-Basin after extended (i.e., decades) storage [2]. The 8-µm bayerite film was used for the initial drying tests.

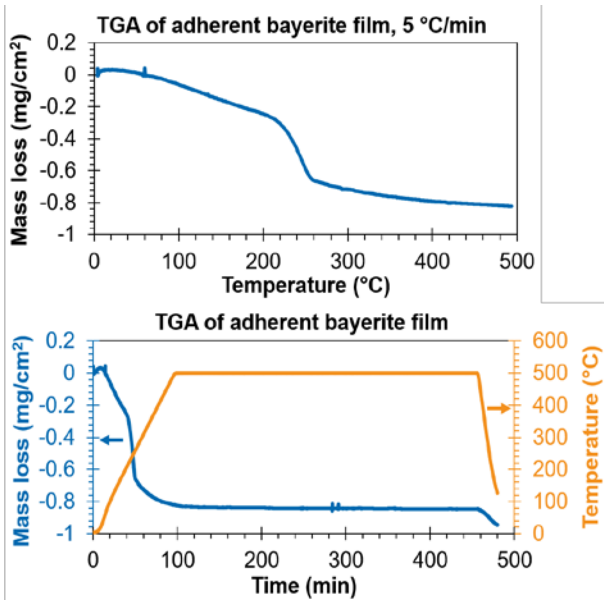

Figure 3. Example TGA results for ~8-µm-thick bayerite film, as a function of (top) temperature during ramp-up to 500°C and (bottom) time for the entire test.

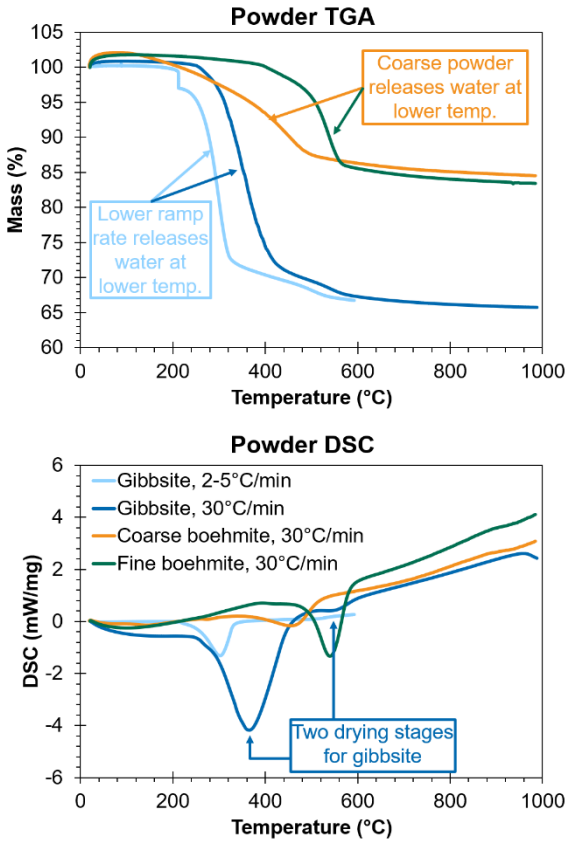

Figure 2. Representative TGA (top) and DSC (bottom) results for gibbsite and boehmite powders.

TGA/DSC tests of (oxy)hydroxide powders resulted in successful conversion of gibbsite powder to boehmite or alumina and of boehmite powders to alumina, depending on the maximum temperature reached. Figure 2 shows some representative TGA and DSC curves for the boehmite and gibbsite powders. At low ramp rates (≤5°C/min), the conversion to boehmite occurred around 300°C (210–340°C). XRD confirmed that boehmite was the only phase detected after tests reaching 450°C. The transition to alumina occurred around 510°C (470–550°C), with XRD detecting only alumina after tests reaching at least 600°C. Boehmite powders dehydrated to alumina at about 400°C (330–460°C) for coarse (77-µm particle diameter) powder and about 490°C (420–520°C) for fine

(0.7-µm particle diameter) powder. For all powders tested, the maximum percent mass loss after drying to high temperature slightly exceeded the theoretical mass loss for complete dehydration of the stoichiometric (oxy)hydroxide to alumina, which is likely attributable to physisorbed water in the powder.

For TGA of adherent (oxy)hydroxide films, the mass loss per unit surface area increased with increasing temperature for all temperatures tested (200, 220, 260, and 500°C). The final mass losses per unit surface area were approximately 0.95 mg/cm^2 for 6 h at 500°C, 0.84 mg/cm^2 for 4 h at 260°C, 0.60 mg/cm^2 for 24 h at 220°C, and 0.51 mg/cm^2 for 24 h at 200°C. For a 500°C, 6-h hold, the mass losses appeared to saturate after approximately 1 hour at temperature, suggesting full dehydration to alumina was reached. The mass losses also appeared to plateau before the end of the hold for 200°C test and decreased to a very low rate for the other temperatures, suggesting that these values were likely close to the maximum achievable mass loss at that temperature. An example of the TGA results for a 500°C test is shown in Figure 3. Here, the most rapid mass loss occurred within the range between about 220 and 250°C, providing further evidence that temperatures ≤220°C may be inherently too low to release much of the bound water. Drying resulted in a dramatic change in film morphology. Figure 4 shows planview SEM of post-drying samples for the same, originally ~8-µm-thick bayerite film shown in Figure 1. The initially continuous film cracked into sections on the order of 50 µm square and partially delaminated, with the outermost layer of the film completely flaked off in some regions. The layer exposed under the spalled oxide also displayed prominent cracking, with spacing on the order of 10 µm, but this surface layer appeared to remain completely adhered to the aluminum substrate.

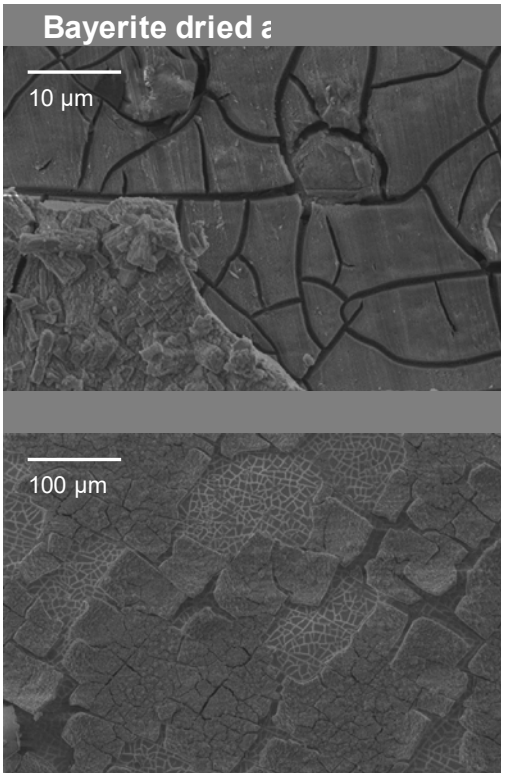

Figure 4. Planview SEM showing post-drying morphology of ~8-µm-thick bayerite films after TGA at (top) 260°C and (bottom) 500°C. Prominent cracking of the film occurred, and some of the oxide spalled off of the surface.

FY2019 Accomplishments

- Thick (up to ~20 micron average), blocky trihydroxide films were produced for use in drying tests via room-temperature water exposure.
- Drying tests have been performed using simultaneous thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) on gibbsite and boehmite powders to identify or confirm key temperature ranges/thresholds for the thermal decomposition reactions and impacts of ramp rate and hold times for drying of isolated, high-surface-area (oxy)hydroxides. The results were used to inform drying of adherent (oxy)hydroxide films.
- Drying tests of adherent (oxy)hydroxide films have been performed. Small pieces of the aluminum specimens with adherent (oxy)hydroxides were cut and studied under TGA. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) were used to examine the morphology and composition, respectively, both pre- and post-drying.

Future Directions

- Radiolysis testing of boehmite films formed by thermal dehydration of trihydroxide films should be conducted to verify whether their gas generation is comparable to that of boehmite films formed directly from aluminum exposure in water at temperatures over 80°C.
- Conclusions from drying behavior (thermal decomposition) and radiolytic yield obtained from investigations of surrogate oxides should be validated using samples cut from actual ASNF exposed to reactor conditions and wet storage (e.g., those sampled in Ref. [2]).

FY 2019 Publications/Presentations

1. Anna L. d'Entremont, Roderick E. Fuentes, Luke C. Olson, Kathryn E. Metzger, Robert L. Sindelar, Oxide Growth and Validation for Aluminum Research Reactor Fuel, Proceedings of Waste Management Symposia 2019, #19422, Phoenix, Arizona. (Conference paper)
2. Anna L. d'Entremont, Roderick E. Fuentes, Luke C. Olson, Kathryn E. Metzger, Robert L. Sindelar, Oxide Growth and Validation for Aluminum Research Reactor Fuel, WM2019 Conference March 3-7, Phoenix, Arizona. (Contributed presentation)
3. Anna L. d'Entremont, Roderick E. Fuentes, Matthew G. Shalloo, Travis W. Knight, Robert L. Sindelar, Thermal Dehydration of Aluminum (Oxy)hydroxides on Fuel Cladding Material, Waste Management Symposia 2020, Phoenix, Arizona (Submitted for paper and presentation).

References

[1] K. Wefers and C. Misra, "Oxides and hydroxides of aluminum," Alcoa Laboratories Pittsburgh, PA Alcoa Technical Paper #19, 1987.

[2] L. C. Olson, C. Verst, A. L. d'Entremont, R. E. Fuentes, and R. L. Sindelar, "Characterization of Oxide Films on Aluminum Materials following Reactor Exposure and Wet-Storage in the SRS L-Basin," Savannah River National Laboratory SRNL-STI-2019-00058, 2019.

Acronyms

ASNF	Aluminum Spent Nuclear Fuel
DSC	Differential Scanning Calorimetry
NMM	Nuclear Materials Management
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

Total Number of Student Researchers

One graduate student (Matt Shalloo) via University of South Carolina subcontract, who worked off-site at USC.