

Characterization of Corrosion Products from Static Cell Testing of AI-SNF Forms

by

T. Adams

Westinghouse Savannah River Company

Savannah River Site

Aiken, South Carolina 29808

A. Duncan

D. Vinson

A document prepared for DOE SNF AND FISSILE MATERIALS MANAGEMENT at Charleston, SC, USA from 9/17/2002 - 9/20/2002.

DOE Contract No. **DE-AC09-96SR18500**

This paper was prepared in connection with work done under the above contract number with the U. S. Department of Energy. By acceptance of this paper, the publisher and/or recipient acknowledges the U. S. Government's right to retain a nonexclusive, royalty-free license in and to any copyright covering this paper, along with the right to reproduce and to authorize others to reproduce all or part of the copyrighted paper.

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-96SR18500 with the U. S. Department of Energy.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report has been reproduced directly from the best available copy.

Available for sale to the public, in paper, from: U.S. Department of Commerce, National Technical Information Service, 5285 Port Royal Road, Springfield, VA 22161,
phone: (800) 553-6847,
fax: (703) 605-6900
email: orders@ntis.fedworld.gov
online ordering: <http://www.ntis.gov/help/index.asp>

Available electronically at <http://www.osti.gov/bridge>
Available for a processing fee to U.S. Department of Energy and its contractors, in paper, from: U.S. Department of Energy, Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831-0062,
phone: (865)576-8401,
fax: (865)576-5728
email: reports@adonis.osti.gov

CHARACTERIZATION OF CORROSION PRODUCTS FROM STATIC CELL TESTING OF AL-SNF FORMS

Thad M. Adams

Westinghouse Savannah River Co.
Savannah River Technology Center
Aiken, SC 29808

Dennis W. Vinson

Westinghouse Savannah River Co.
Savannah River Technology Center
Aiken, SC 29808

Andrew J. Duncan

Westinghouse Savannah River Co.
Savannah River Technology Center
Aiken, SC 29808

ABSTRACT

Aluminum-based spent nuclear fuel from foreign and domestic research reactors is being consolidated at the Savannah River Site (SRS) for ultimate disposal in the Monitored Geologic Repository. The melt-dilute treatment technology has been developed to consolidate fuel assemblies by a melting/casting process in which depleted uranium is added to reduce enrichment below 20% ^{235}U . The melt-dilute product is essentially a binary uranium-aluminum alloy to which neutron absorber materials may be readily added.

The corrosion of uranium-aluminum alloys including neutron absorbers is being investigated in accordance with ASTM C1431-99. Testing was conducted in static cells using surrogates of the melt-dilute treatment product. Characterization of the uranium-aluminum alloys, including absorbers, in these static cell tests with high pH modified J-13 water at 90°C showed the formation of aluminosilicates and uranyl-silicates.

I. BACKGROUND

Approximately 20 metric tons heavy metal of aluminum-based spent nuclear fuel (Al-SNF), or approximately 15,000 assemblies from foreign and domestic research reactors, are being consolidated at the Savannah River Site. The melt-dilute treatment has been developed for ultimate disposal of these fuels, most of which contain highly enriched uranium (HEU) (>20% ^{235}U), in the monitored geologic repository (MGR).ⁱ This alternative for

disposition of the Al-SNF has been selected as the preferred alternative through the EIS process.ⁱⁱ The proposed waste package will co-dispose a canister containing the melt-dilute SNF (MD-SNF) form with several borosilicate glass logs of defense high-level waste (DHLW). The melt-dilute form is essentially a binary uranium-aluminum alloy near the eutectic composition (13.2%U-Al). This results in a heterogeneous microstructure of aluminides in an aluminum matrix.

An issue in the disposal of spent fuel in the repository is the potential for achieving a criticality event. Analyses of degraded configurations of the MD-SNF form at 20% ^{235}U enrichment^{iii-iv} indicate that the reactivity of some degraded configurations exceeds the limit of $k_{\text{eff}} = 0.95$.^v Among the possible methods available to reduce the reactivity of the SNF forms is to control the amount of fissile material disposed of in a single waste package and to integrate neutron absorbers with the melt-dilute form. Neutron absorbers that are added to uranium-aluminum alloys must be metallurgically compatible to successfully achieve a fabrication process. Additionally, these absorbers must not readily separate under corrosion degradation scenarios in order to maintain criticality control.

The degradation behavior of the MD-SNF form, including degradation rate and degradation product formation, as well as the behavior of the neutron absorbing materials, including degradation product formation and relative solubility, are important characteristics used to demonstrate MD-SNF/neutron absorber

compatibility and long-term criticality control in the repository. Testing has been performed to fully characterize the degradation products of the MD-SNF form with neutron absorbing material additions under static aqueous conditions relevant to the proposed repository.

Previous work done at Argonne National Laboratory on irradiated U-Al fuel coupons documented the formation of silica-substituted aluminum hydrogels, uranyl-silicates, uranyl-oxyhydroxides and becquerelite in drip tests conducted in equilibrated natural J-13 water at 90°C^{vi}

II. DESCRIPTION OF WORK

Corrosion Test Program

A testing protocol guide to support the repository disposal of aluminum-based spent nuclear fuel forms was recently issued by ASTM.^{vii} Corrosion testing per this guide is ongoing. The corrosion testing to date has included vapor, static, single-pass flow, and electrochemical tests on uranium-aluminum and surrogate melt-dilute materials.

Static coupon tests were performed in synthetic J-13 water spiked with sodium-hydroxide to produce a pH of approximately of 11. Table 1 displays the nominal concentration of the starting sodium hydroxide spiked J-13 waters. These tests were run at 90°C for 3 month exposures. The goal for these test was to identify/characterize the type of corrosion products formed during degradation of U-Al alloys expected from the melt-dilute treatment technology. Several different alloy compositions were examined in these test and they are given as follows: eutectic U-Al, U-Al-3Gd, U-Al-3Hf, U-Al-1.5Gd-1.5Hf, U-Al-1.5Si, and U-Al-1.5Si-3Gd.

Table 1. Nominal Composition for Sodium-hydroxide Spiked Synthetic J-13

<u>Species</u>	<u>Concentration (ppm)</u>
Al	0.87
B	1.48
Ba	14.1
Ca	10.0
Cd	<0.0028

Co	<0.0088
Cr	<0.01
Cu	0.02
Fe	0.04
Li	<0.02
Mg	1.31
Mn	<0.0018
Mo	<0.02
Na	1670
Ni	0.03
P	0.34
Pb	<0.138
Si	40.1
Sn	<0.052
Sr	0.03
Ti	<0.028
V	<0.026
Zn	0.16
Zr	<0.0096
La	<0.14
Ag	<0.06

Characterization of the corrosion products formed on the surfaces of the surrogate U-Al alloy coupons were analyzed using x-ray diffraction(XRD) and scanning electron microscopy (SEM). For the SEM analysis, the coupons surfaces as well as cross-section were examined. Energy Dispersive Spectroscopy was performed on these samples to identify the elemental species in the corrosion products.

III. CHARACTERIZATION RESULTS

Eutectic Al-U Alloy

Characterization of cross-sectioned samples from a eutectic U-Al coupon was performed using SEM and EDS. Figures 1 and 2 show coss-section SEM image of the coupon. EDA analysis from points A and B resulted in determination of alumino-silicates and uranyl-silicates as shown in Figures 3 and 4. XRD results were inconclusive as to identifying the exact alumino-silictae and uranyl-silicate due to a relatively thick aluminum-oxide layer on the surface of the sample.

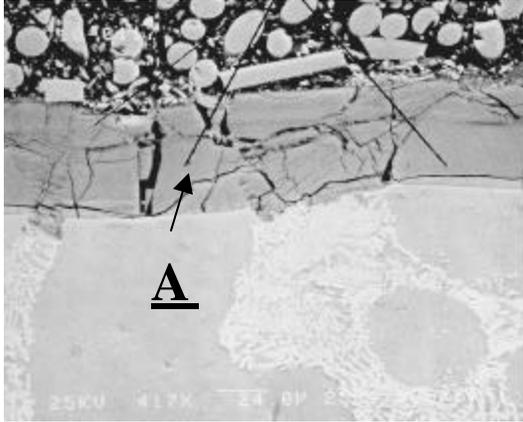


Figure 1. Eutectic U-Al Alloy with Corrosion Product Layer

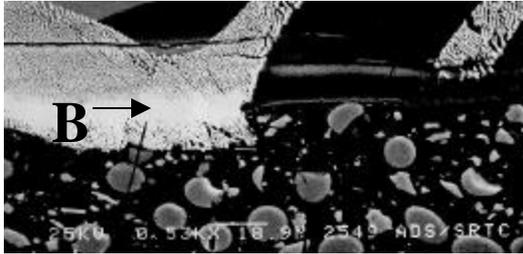


Figure 2. Corrosion Product Layer on a Eutectic U-Al Alloy

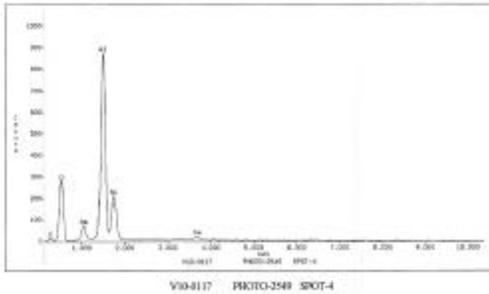


Figure 3. EDS scan from point A in Figure 1 Indicating Alumino-silicate Corrosion Product

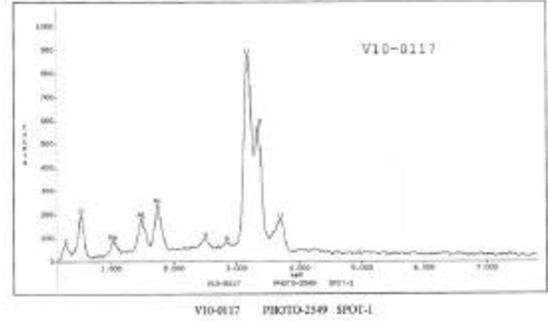


Figure 4. EDS scan from point B in Figure 2 Indicating Uranyl-silicate Corrosion Product

Al-U-3Gd Alloy

Examination of the eutectic U-Al doped with 3wt% gadolinium using SEM showed a similar corrosion product microstructure to that of the base eutectic U-Al alloy, Figure 5. Analysis of the corrosion product regions with EDS once again showed the presence of Al-oxides, alumino-silicates, and uranyl-silicates, Figures 5 and 6. The uranyl-silicate corrosion product in these samples appears interdispersed within the alumino-silicate products, Figure 7. A possible explanation for this occurrence is that formation of the alumino-silicate begins from the Aluminum matrix trapping UAl_x particles, which subsequently undergo the reaction to form the uranyl-silicates.

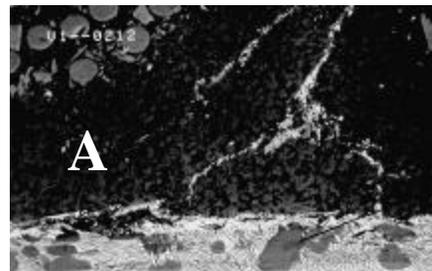


Figure 5 SEM Photomicrograph of Corrosion Product Layer on a U-Al-Gd Alloy

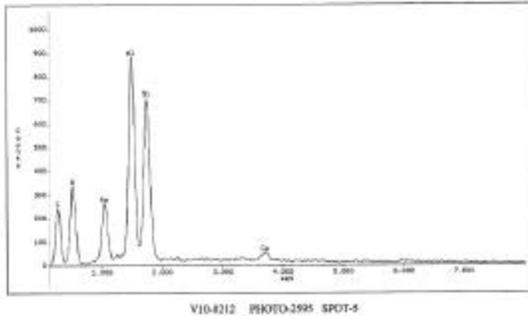


Figure 6. EDS scan from point A in Figure 5 Indicating Alumino-silicate Corrosion Product



Figure 7. SEM Photomicrograph of Uranyl-silicate Corrosion Product

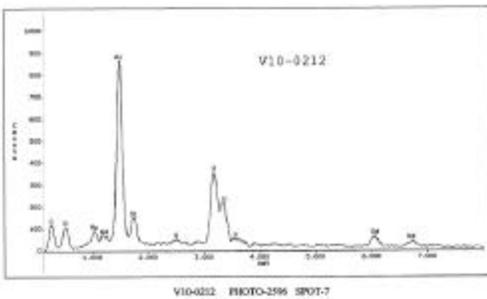


Figure 8. EDS Analysis of Uranyl-silicate Corrosion Product

Al-U-3Hf Alloy

The U-Al-3Hf alloy coupon was coupled to an A36 carbon steel coupon during testing to simulate the melt-dilute Al-SNF form in a carbon steel liner. Characterization of this coupon following exposure showed similar microstructural features to the previous exposed samples with the exception of small patches of particles the alumino-silicate

layer that appeared as “feathery needles”, Figure 8. EDS analysis of these “feathery needles” returned a result of an iron-based compound, Figure 9. XRD results preliminarily identified the compound as “green rust” $Fe_6(OH)_{12}(CO_3)$. These “green rust” particles are < 1 μm in size.

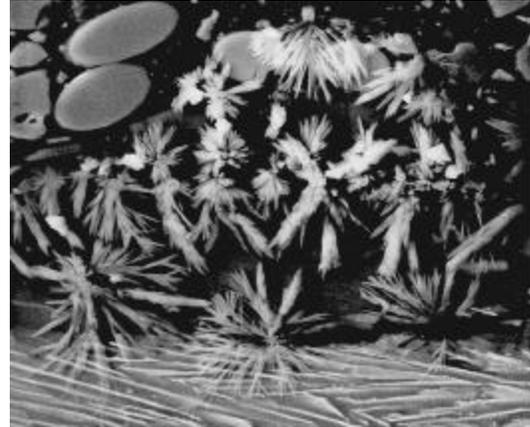


Figure 9. SEM Photomicrograph of “feathery needle” Corrosion Product on U-Al-3Hf Coupled to A36 Carbon Steel

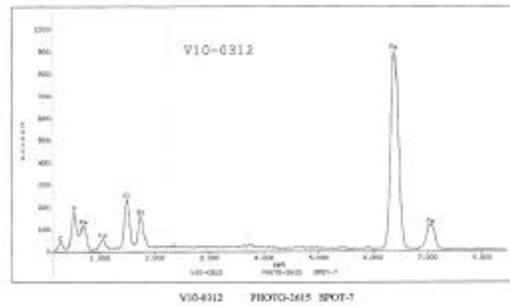


Figure 10. EDS Analysis Indicating an Fe-O-C Compound Identified as “green rust”-- $Fe_6(OH)_{12}(CO_3)$.

Al-U-1.5Gd-1.5Hf Alloy

The U-Al-1.5Gd-1.5Hf alloy was also coupled to A36 carbon steel during testing. Characterization of this sample using SEM and EDS showed the formation of uranyl-silicates, alumino-silicates, and “green rust” on the surface of the sample, Figures 10-15. It is interesting to note the presence of gadolinium in the uranyl-silicate corrosion product. This indicates that collocation of the neutron absorber (Gd) with the initial UAl_x particle in the starting microstructure remains even after reaction to form the uranyl-silicate.

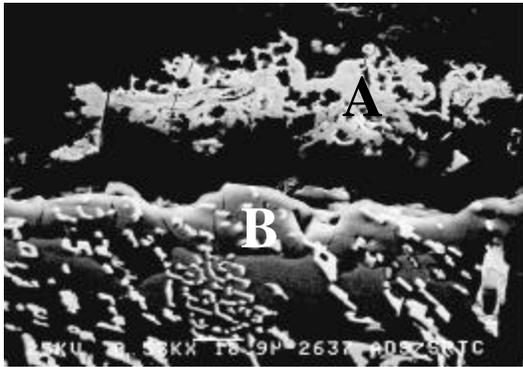


Figure 11. SEM Image of Corrosion products on a U-Al-1.5Gd-1.5Hf Alloy

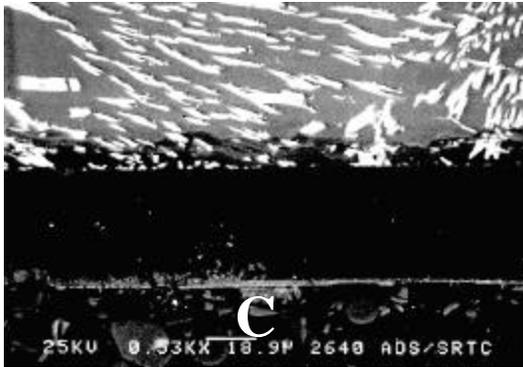


Figure 12. SEM Image of Thin Corrosion Product Layer

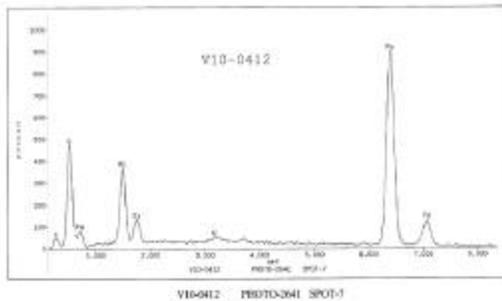


Figure 13. EDS Scan from point C in Figure 12—Indicating “green rust” corrosion product layer

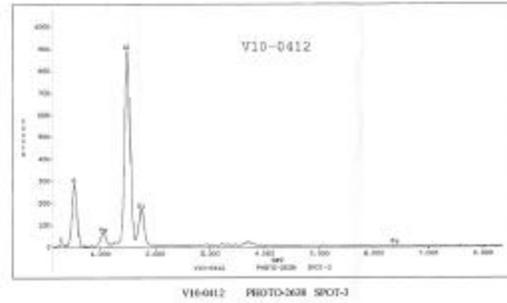


Figure 14. EDS Scan from point B in Figure 11—Indicating aluminosilicate corrosion product layer

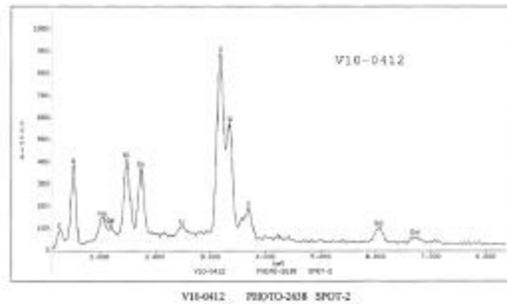


Figure 15. EDS Scan from point A in Figure 11—Indicating uranyl-silicate corrosion product layer

IV. SUMMARY

Characterization of the uranium-aluminum alloys, including neutron absorbers, in these static cell tests with high pH modified J-13 water at 90°C showed the formation of aluminosilicates and uranyl-silicates.

Preliminary indications from these tests demonstrate that gadolinium remains co-located with uranium containing corrosion products. This provides a technical basis for a waste form involving integral neutron absorbers.

REFERENCES

- i T. M. Adams, H. B. Peacock, Jr., R. L. Sindelar, N. C. Iyer, W. F. Swift, F. C. Rhode, and H. M. Brook, “Melt-Dilute Treatment Technology for Aluminum-Based Research Reactor Fuel,” Proceedings of the ANS-DOE Spent

Nuclear Fuel and Fissile Management,
pp. 41-45, 2000.

- ii “Savannah River Site Spent Nuclear Fuel Management Final Environmental Impact Statement,” USDOE-Savannah River Operations Office, DOE/EIS-0279, 2000.
- iii S. M. Revolinski, “Criticality Evaluation of DOE SNF Codisposal Canister with Melt and Dilute MTR Fuel,” Westinghouse Safety Management Solutions, WSMS-CRT-98-003, Rev. 03, 1998.
- iv B. A. Baranko, “Phase II Criticality Evaluation of Melt-Dilute Al-SNF and DHLW Codisposal,” Westinghouse Safety Management Solutions, N-CLC-L-00040, 1999.
- v US Code of Federal Regulations, Chapter 10, Part 60.
- vi M. D. Kminski and M. M. Goldberg, “Aqueous Corrosion of Aluminum-Based Nuclear Fuel,” accepted for publication in the Journal of Nuclear Materials, 2002.
- vii ASTM C1431-9, “Standard Guide for Corrosion Testing of Aluminum-Based Spent Nuclear Fuel in Support of Repository Disposal,” American Society for Testing and Materials, August 1999.