

THE INFLUENCE OF COPPER ON ZIRCALOY SPENT FUEL CLADDING DEGRADATION
 UNDER A POTENTIAL TUFF REPOSITORY CONDITION

H. D. Smith
 Westinghouse Hanford Company
 P. O. Box 1970
 Richland, WA 99352

ABSTRACT

The purpose of this paper is to report the results of an experiment designed to detect the influence of copper on zircaloy spent fuel cladding degradation in a tuff repository environment. The results show that there are no indications of discrete copper-containing phases forming as part of a developing oxide film on the zircaloy and that it is estimated that it would take more than 30,000 years to penetrate the cladding by oxidation. Both metallography and the scanning electron microscope suggest that the effects of corrosion due to exposure to the model repository environment are not significant.

INTRODUCTION

Copper and copper alloys are being considered for use in a tuff repository. The compatibility of a copper waste package container and the Zircaloy cladding on spent fuel, however, has been questioned essentially because of two observations: first copper ion has been observed to accelerate zirconium alloy corrosion in acid environments, as does ferric iron;^(1,2,3) and second, a phenomenon called "crud-induced localized corrosion," is observed in some BWRs (Boiling Water Reactors) where through-the-wall corrosion pits develop beneath copper-rich crud deposits.⁽⁴⁾ This paper reports the results of an experiment designed to detect the influence of copper on Zircaloy spent fuel cladding degradation in one possible repository environment.

The potential tuff repository environment being modeled is expected to develop as a result of radiolysis of humid air at an air/water interface,^(5,6) after the repository rock and waste package have cooled to below the boiling point (more than several hundred years after emplacement). Radiolysis-generated nitric acid would dissolve in available water and the water in contact with copper would produce a copper nitrate solution. Depending on the amount of water available, a relatively concentrated solution may develop. It is recognized that this repository environment differs considerably from those conditions in which copper is known to deleteriously affect the corrosion characteristics of zirconium alloys; see Table I below. However, the degree of interaction between copper and Zircaloy spent fuel in a repository environment must be understood before copper or copper alloys can be properly evaluated as candidate container materials.

TABLE I

A COMPARISON OF SOME EXPECTED TUFF REPOSITORY ENVIRONMENTAL CONDITIONS WITH THOSE IN WHICH COPPER HAS BEEN OBSERVED TO HAVE INFLUENCED ZIRCALOY CORROSION

	<u>Simulated Tuff Repository Condition</u>	<u>BWR(8,9)</u>	<u>Acid Corrosion</u>
Temperature	~90°C	<u>290-300°C</u>	20 - >100°C
log P _{O₂} (atm.)	-0.7	<u>-7.0</u>	-0.7
pH	4.5 (Conc. Cu(NO ₃) ₂) to 9	5.5-7.5	<u><3</u>
Radiation Dose Rate	~4 R/hr	<u>~10⁸ R/hr</u>	0

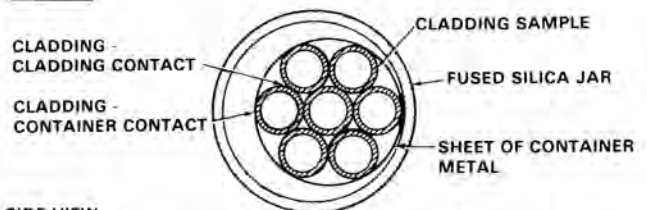
*Highlighted items (underlined) indicate significant differences from repository conditions.

EXPERIMENTAL SETUP AND PROCEDURE

In this experiment a 0.1 M copper nitrate solution held at 90°C was used to accelerate the localized corrosion phenomenon of concern. This high nitrate concentration exceeds that which would be expected to occur in the repository, but was considered a useful starting place. The copper container incorporating spent fuel was modeled using a small bundle of Materials Characterization Center's Approved Testing Material ATM 101(7) spent fuel rod sections (4 1/2" long) tied together by a 10-mil-thick, two-inch-wide copper foil wrap, certified 99.999 wt % pure. Three rod sections in each seven-section bundle were polished on one side to remove the oxide film, increasing the ability of the Zircaloy spent fuel cladding to react with the environment. Two such bundles were assembled, one for a two-month experiment, and one for a five-month experiment. (See Fig. 1.) Each bundle was immersed half-way up on the copper foil wrap in 0.1 M $\text{Cu}(\text{NO}_3)_2$ solution in a jar, and the temperature was maintained at $90^\circ\text{C} \pm 2^\circ\text{C}$ by placing the jars in an oil bath. The jars are made of fused silica and the lids are fabricated from Pyrex* glass parts.

Each bundle contained approximately 400 g of spent fuel, which resulted in a gamma radiation dose rate of about 1000 R/hr near the surface of the

TOP VIEW



SIDE VIEW

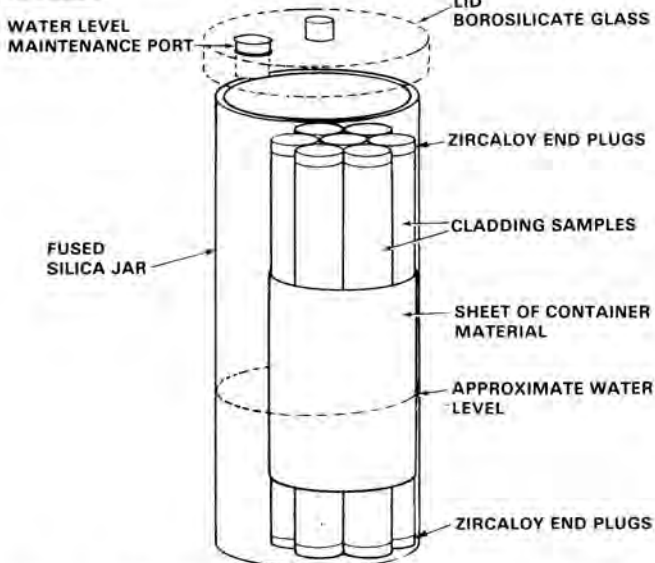


Fig. 1. Schematic of Corrosion Cell Used for the 2-Month and 5-Month Experiments. Copper foil wrap with copperwire tie holds bundle together. Zircaloy plugs are press fit to mechanically seal each cladding section.

*Trademark of Pittsburgh Corning, Pittsburgh, PA.

bundle. This radiation field caused the fused silica jars to turn black, and it also caused the atmosphere in the jars above the nitrate solution to have a higher conductivity than is normally observed for humid air at 90°C; i.e., the resistance measured between two wires separated by 1.03 cm was $\sim 5 \text{ M}\Omega$ versus $>20 \text{ M}\Omega$ in air outside the jar. Fluid specimens were removed from each jar through the port in the lid at regular intervals during the experiment. During the course of the 2- and 5-month experiments, the solution pH remained at ~ 4.5 , while the concentration $[\text{Cu}(\text{NO}_3)_2]$ dropped to approximately one-half the original level, and the Zr content of the solution remained below the detectability limit of 25 ppb. The zirconium determination was made via inductively-coupled plasma optical emission spectroscopic analysis as soon as possible after a solution sample had been removed from the experiment (i.e., within 15 minutes). The fluid removed was replaced using a stock solution, volume for volume. Occasionally some evaporative loss was observed, apparently due to incomplete sealing of the port in the lid. This loss was made up with deionized water, volume for volume.

The experiments were terminated by taking final solution samples after 2 and 5 month periods, respectively, then removing the jars from the oil bath. Each bundle was removed from its jar and placed on a piece of clean, absorbent material to dry. Next it was photographed, disassembled, and each part photographed separately.

SAMPLE EVALUATION AND EXPERIMENTAL RESULTS

Each bundle became encrusted with a green compound that was identified by x-ray diffraction analysis (XRD) as $\text{Cu}_2(\text{OH})_3\text{NO}_3$ (copper hydroxide nitrate, also known as basic cupric nitrate and Gerhardite) during the experiment. The bulk of the deposit was above the water line and on the copper wrap as shown in Fig. 2, which presents before and after photographs of the 2-month experiment. The copper wrap was partially oxidized to Cu_2O (XRD) and was less flexible than the original copper. The bundle from the 5-month experiment appeared essentially the same as that from the 2-month, but the oxidation of the copper wrap had clearly gone further. When the copper wrap was removed, the cladding sections appeared unaffected, except that they had some of the same encrustation by the green copper compound. The polished areas also appeared unaffected except for a small amount of the copper compound that was mentioned above. More significantly, the polished metal was still bright and did not show any change of color that would suggest the development of a corrosion scale.

Ring samples were taken from the upper, middle and lower part of the cladding sections that had a polished strip on one side, for instrumental evaluation. Each ring was first defueled and then divided into several sections for different modes of instrumental analysis, as indicated in Fig. 3.

Metallography

Metallography was used to survey the part of the circumference of the cladding section that was still covered with the original oxide. A polished section was produced which allowed the oxide film and the oxide-metal interface to be viewed in cross section. The section was then surveyed for unusual structures (as compared to archive material) that might indicate localized corrosion, and deposits of compounds or metal that might indicate an interaction between the copper and the spent fuel cladding. Nothing unusual was observed. A typical section is shown in Fig. 4.

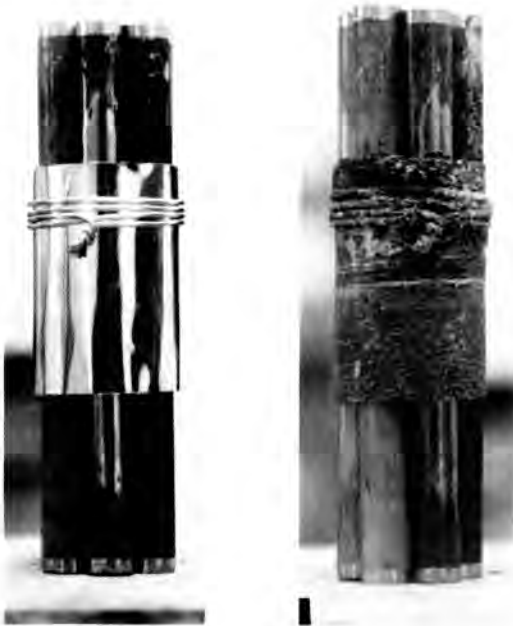


Fig. 2. Before and after Photographs of the Cladding Bundle Used in the 2-Month Experiment. Discontinuity in texture of deposits about half way up on the copper wrap indicates the water level during the experiment. Note that the polished cladding is still shiny after two months.

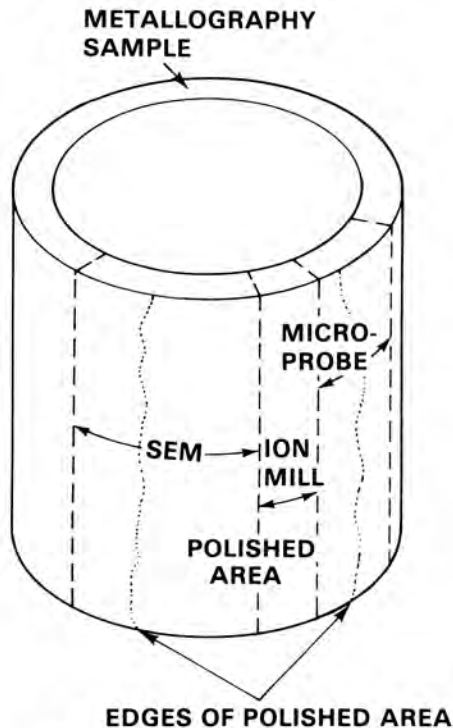


Fig. 3. Sectioning Diagram for Each Ring Specimen (see Fig. 2). Ring segments were evaluated via SEM, Auger/ion milling, electron microprobe, and metallography.

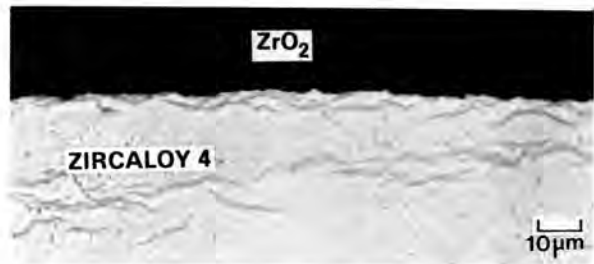


Fig. 4. Example of Thick Films on H. B. Robinson Spent Fuel Cladding From the 5-Month Experiment.

Electron Probe Analysis

Electron probe samples were prepared in such a manner that any copper accumulations that might have occurred in the oxide film or on the metal surface could be observed in cross section. The samples were examined for copper via the probe using line profiles from the surface of the oxide film to the oxide-metal interface, and by point analyses across the oxide film and at the oxide-metal interface. No copper was detected even though the sensitivity of the line profiles was 0.1-1 wt% and those of the point analyses were about 0.1 wt%.

Scanning Electron Microscopy

SEM (scanning electron microscope) examination was performed on nine specimens each from the 2-month and the 5-month experiments. The specimens for SEM evaluation included polished and unpolished areas and the oxide/metal interface at the boundary between the two areas. These three regions were each surveyed photographically in at least five places on each specimen. In addition, energy dispersive analysis of fluorescence x-rays was used to perform semi-quantitative elemental analysis.

Figure 5 shows SEM micrographs of a specimen of an oxide film from the 2-month experiment which is also representative of what was seen after 5 months. There are many surface features on the cladding that are the result of the cladding manufacture and subsequent incorporation into a fuel assembly; these are visible



Fig. 5. Scanning Electron Micrographs of Cladding Samples With Thin Oxide From the 2-Month Experiment: a) Total specimen with well defined boundary between polished (right) and unpolished (left) areas, b) High magnification SEM micrograph of boundary showing oxide (dark) and metal (light) areas. Notice that the oxide-metal interface shows no topographical expression.

on the unpolished areas of the SEM specimen as scratches and grooves. The oxide surfaces of similar oxide specimens which were observed to have suffered abrasion during polishing procedures, have spalled in areas, giving a pitted appearance. The polished areas (on the right--lighter surface) display a variety of polishing and handling artifacts, i.e., scratches, grooves, etc. At a magnification of 1000-2000X an even greater array of scratches, grooves, crevices and pits are observed (see Fig. 5).

In spite of the topographic background outlined above, there are features that can be examined in detail for signs of active corrosion processes. At the boundary between the polished and unpolished areas, the oxide/metal interface is the very irregular boundary between the dark, thinned oxide (ZrO_2) and the metal substrate. The high magnification SEM micrographs show that wherever this boundary is clearly visible, there is no hint of oxide metal separation, etching, or pitting in either the 2- or 5-month experiment.

Surface analyses using the SEM energy dispersive x-ray system have, in general, indicated only zirconium with minor amounts of iron and silicon. The presence of silicon is probably due to deposition of silica from solution which originated from the fused silica jar. The iron was observed only occasionally, in small amounts, and probably indicates the presence

of a thin film of "crud" on top of the oxide. Out of all the specimens evaluated (18 total - nine from 2-month and nine from 5-month experiments), copper was observed only once in a $15 \times 30 \mu m$ finely crystalline deposit on the oxide film of spent fuel, which is believed to be a small deposit of the $Cu_2(OH)_3NO_3$ compound observed at other locations. The general lack of tin, chromium and iron in the SEM energy dispersive x-ray spectrum is believed to be due to the fact that these elements are largely tied up in discrete intermetallic phases that make up a small volume of the alloy, and if they are not right at the surface in sufficient quantity, they would not produce a detectable x-ray signal.

Auger/Ion Milling

Specimens of pre-experiment polished Zircaloy cladding from both the 2-month and 5-month experiments have been characterized via Auger Electron Spectroscopy with ion milling. Elemental concentration profiles were produced of the oxide corrosion film as a function of time, which corresponds to depth into the Zircaloy metal substrate on which the film is formed. An Auger spectral survey of the surface of the cladding specimens is taken prior to sputtering. Another survey is performed after 30 seconds of sputtering. This is followed by the depth profiling of the oxide corrosion film, and then a post-profile survey is taken.

A time-versus-concentration profile can be interpreted as a depth profile if there is a basis for estimating milling (sputtering) rate. This is established prior to characterization of any of the samples by sputtering a 1000 \AA Ta_2O_5 film to establish the milling characteristics of the ion beam, and this is repeated after a series of sample characterizations is complete to determine the beam stability. It took about 13 minutes to mill through the 1000 \AA Ta_2O_5 film, and this is equivalent to a sputtering rate of 77 \AA/minute . It was assumed that zirconium oxide also milled at 77 \AA/minute . The validity of this assumption is difficult to ascertain from the available literature, so a direct comparison between the milling rates of tantalum and zirconium oxide films is planned.

Depth profiles were completed on three specimens from the 2-month experiments and on eight from the 5-month experiment to see: 1) if copper concentrations had developed anywhere within the corrosion film or at the metal/oxide interface and, 2) to approximately determine the thickness of the oxide film to see if the copper-containing environment had substantially increased the corrosion rate of the Zircaloy cladding over that produced by a typical groundwater environment. (Data to make this comparison will soon be available.) The oxide thicknesses are given in Table II. The values given in Table II are about a factor of 3 higher than the thicknesses calculated from higher temperature oxidation models extrapolated to these experimental conditions. However, the relative milling rate of tantalum metal and tantalum oxide has been measured to be about 1:4(10,11) whereas zirconium and zirconium oxide have been observed to mill at similar rates (i.e., it is possible to ion mill ultra-thin sections of zirconium oxide and zirconium metal side by side). Further sputtering yields of tantalum and zirconium are observed to be about equal(11) Hence, tantalum oxide may sputter (mill) considerably more rapidly than zirconium oxide. In addition the "polished Zircaloy" had a 1 micron ($10,000 \text{ \AA}$) diamond polish, which is not a "flat" surface at the 1000 \AA level, and this may have resulted in an apparent "smeared" zirconium oxide/Zircaloy interface. Therefore, it is possible that

TABLE II

AVERAGE OBSERVED ION MILLING TIME TO ACHIEVE A 90% DECREASE IN SURFACE OXYGEN CONCENTRATION AND AN EQUIVALENT INCREASE IN SURFACE ZIRCONIUM CONCENTRATION

	Sample*	Milling Time (Min)	Ta ₂ O ₅ Equivalent Thickness
2-Month Exp.	P2	3.8	370 ± 70 Å
	U3	5.7	
	Q1	4.9	
5-Month Exp.	J1	4.2	420 ± 70 Å
	J2	6.4	
	J3	6.9	
	K1	5.2	
	K2	5.2	
	K3	4.7	
	M2	6.0	
	M3	5.3	

*The sample designation indicates cladding section (letter) and position on cladding section (number). The number indicates:
 1 - cladding in contact with air
 2 - cladding in contact with solution and copper wrap
 3 - cladding in contact with solution only.

the oxide film on the polished Zircaloy cladding is actually a factor of 3-4 thinner than inferred in Table II.

Figure 6 shows the derivative (dN/dE) of the Auger electron flux as a function of energy, taken prior to milling (pre-sputter survey), after 30 seconds of milling (post-sputter survey), and after the depth profile was produced (post-profile survey). The data acquisition time was 5 minutes for each spectrum. Each peak is characteristic of a particular energy of Auger electrons emitted from the surface.⁽¹²⁾ The energies of the Auger electrons for elements observed on these specimens are indicated at the top of the figure. Elements such as sodium, calcium, oxygen (partly) and carbon (partly) are probably present as surface contamination. Carbon, nitrogen, oxygen, iron and zirconium are known to be present in the Zircaloy, and may be segregated into discrete phases or incorporated into the oxide film. Argon is apparently implanted in the surface during the ion milling procedure.

Copper is the element in question with respect to its possible influence on the corrosion rate of Zircaloy. There is no evidence that copper is present in any of the samples as anything other than one of several contaminants on the specimen surface along with sodium, calcium, etc. Thirty seconds of milling decreases the copper signal to below detectability (~1%) in every case.

The zirconium level increased and the oxygen level decreased with depth, as might be expected. Elements such as carbon and nitrogen could be present both as contamination and part of the Zircaloy. Dooley⁽¹³⁾ has observed carbon, nitrogen and calcium among other elements in the Auger spectrum of Zircaloy-4; hence, their presence here is not a new observation.

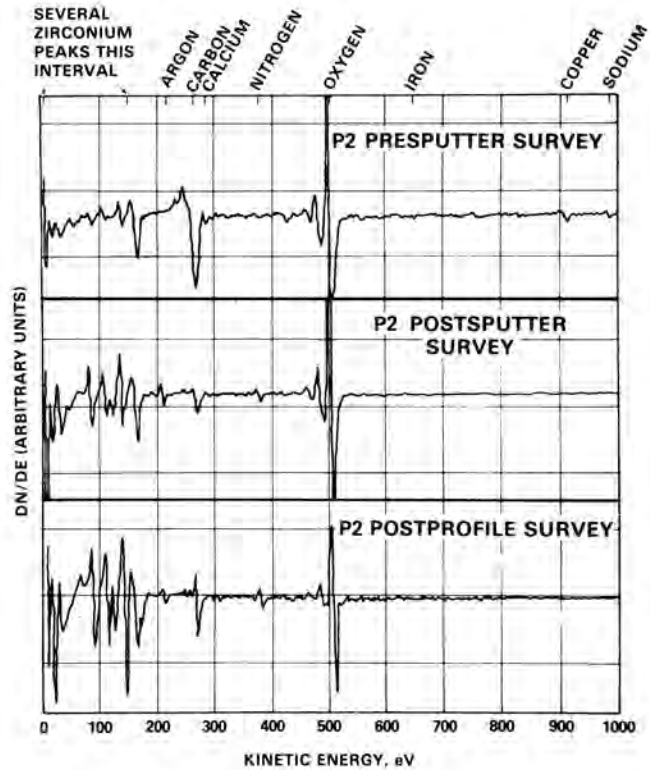


Fig. 6. Auger Electron Spectrum For Specimen P2 From the 2-Month Experiment. Copper, sodium, and calcium seem to be present on the undisturbed surface and are quickly removed by sputtering, i.e., the surface after 30 seconds of sputtering (Post-sputter surface) doesn't show these elements. All 12 specimens from 2- and 5-month experiments exhibited very similar spectrums.

DISCUSSION AND CONCLUSIONS

Two important observations can be made from these results. First, there aren't any indications of discrete copper-containing phases forming as part of a developing oxide film on the Zircaloy. The copper observed was on the oxide surface but not, apparently, part of the oxide film. Only low levels of copper (below the detection limits) could have been present in the oxide or at the oxide/metal interface. Second, about 50 Å of oxide film growth occurred during the time interval between two and five months. The calculated oxidation rate for Zircaloy under aqueous conditions at 90°C would produce an oxide film about 115 Å thick after two months and an oxide film about 145 Å thick after five months, including an initial ~50 Å formed in laboratory air, on the polished metal areas prior to the experiment.^(14,15) An even lower rate of growth is expected for the areas with a well-developed oxide film.^(14,16) This difference is about the same as we observed experimentally, the scatter in the data is larger than the difference, and the absolute values are about 3-4 times less, possibly for reasons already discussed. At this rate (≤ 200 Å metal/year) it would take ~30,000 years

to penetrate the cladding, and the oxidative corrosion rate with a thicker oxide film in place is expected to be even less than 200 Å/year.

Both metallography and SEM investigations suggest that effects of corrosion due to exposure to the model (Cu(NO₃)₂) repository environment are not significant. SEM evaluation of the polished areas of several cladding sections reveal no phenomenon that could be unambiguously ascribed to corrosion, i.e., pits, grooves, etc. In particular the SEM micrographs show no modification of the metal/oxide interface along the boundaries of the polished areas, where corrosion might cause raised edges or might etch the metal relative to the thin oxide film. The oxide/metal interface at the edge of the polished areas was so tight that no topographical expression was observed in any of the specimens at magnifications to 2000X.

The fact that no well-defined concentrations of copper in metallic or compound form were identified in contact with the Zircaloy or incorporated into the oxide film, coupled with the lack of observed physical effects on the Zircaloy cladding, strongly suggest that under the conditions of the experiment no significant electrochemical corrosion processes involving copper were active. The thickness of the oxide film, which had developed on the areas of the spent fuel cladding which were previously polished, was similar to the thickness of a film that would be expected to form under similar conditions without copper present.

The conditions in which copper has been observed to be involved in Zircaloy cladding corrosion, i.e., strongly acid solutions containing Cu⁺² ion(1) and the BWR environment in which the presence of copper-containing components in the cooling water circuit has brought about "crud-induced localized corrosion,"(4) are both quite different from the potential tuff repository conditions (see Table I). It is thus perhaps not too surprising that the copper-related corrosion mechanisms observed in such environments were not found here.

ACKNOWLEDGMENT

Prepared by Nevada Nuclear Waste Storage Investigations (NNWSI) Project participants as part of the Civilian Radioactive Waste Management Program. The NNWSI Project is managed by the Waste Management Project Office of the U.S. Department of Energy, Nevada Operations Office. NNWSI Project work is sponsored by the Office of Geologic Repositories of the DOE Office of Civilian Radioactive Waste Management.

The author is pleased to acknowledge the following individuals of the Hanford Engineering Development Laboratory for their contributions to this work. The experiment was set up and run by Dale Archer. Clyde Chamberlin assembled the experimental specimens and prepared samples for post-experiment evaluation. Bernard Mastel performed the SEM surveys. The surface analyses and the chemical profiles produced via ion milling and Auger electron spectroscopy were the result of Robert Stromatt's efforts.

REFERENCES

1. J. N. Wanklyn, "Recent Studies of the Growth and Breakdown of Oxide Films on Zirconium and Its Alloys," *Corrosion of Zirconium Alloys*, ASTM Spec. Tech. Publ. No. 368, 1964.
2. Te-Lin Yau, "Performance of Zirconium and Columbium in Simulated FGD Scrubber Solutions," *NACE Corrosion/83*, Paper 191, 1983.
3. Te-Lin Yau, "The Corrosion Properties of Zirconium Alloys in Chloride Solutions," *NACE Corrosion/83*, Paper 26, 1983.
4. M. O. Marlowe, J. S. Armijo, B. Cheng and R. B. Adamson, "Nuclear Fuel Cladding Localized Corrosion," *Light Water Fuel Performance, Orlando, Florida, DOE/NE/34130-1*, April 1983.
5. W. G. Burns, et al., "Radiation Effects and the Leach Rates of Vitriified Radioactive Waste," *Nature*, V. 295, pp. 130-132, 1982.
6. H. D. Smith, *Zircaloy Cladding Corrosion Degradation in a Tuff Repository*, HEDL-7455, Rev. 1, Hanford Engineering Development Laboratory, Richland, WA, July 1985.
7. J. O. Barner, *Characterization of LWR Spent Fuel MCC-Approved Testing Material--ATM 101*, PNL-5109, Rev. 1, Materials Characterization Center, June 1985.
8. B. Cheng, et al., "Development of a Sensitive and Reproducible Steam Test for Zircaloy Modular Corrosion," *Amer. Soc. for Testing and Materials*, 7th International Conf. on Zirconium in the Nuclear Industry, Strasbourg, France, June 24-27, 1985.
9. A. B. Johnson, et al., "Nature of Deposits on BWR and PWR Primary System Surfaces in Relation to Decontamination," *Water Chemistry II*, Brit. Nuc. Eng. Soc. and Royal Soc. of Chem., Bournemouth, October 14-17, 1980.
10. G. Betz and G. K. Wehner, "Sputtering of Multi-component Materials," *Topics in Applied Physics*, ed. R. Behrisch, V. 52, p. 78, Springer-Verlag, 1983.
11. H. H. Anderson and H. L. Bay, "Sputtering Yield Measurements," *Topics in Applied Physics*, ed. R. Behrisch, V. 47, pp. 179, 184, Springer-Verlag, 1981.
12. L. E. Davis, et al., "Handbook of Auger Electron Spectroscopy," 2nd Ed., Physical Electronics Industries, Inc., Eden Prairie, MN, 1976.
13. G. J. Dooley, III, "Surface Segregation Studies in Alloys Using Auger Electron Spectroscopy," *Jour. of Vac. Sci. and Technology*, Vol. 9, No. 1, 1972.
14. A. J. Rothman, *Potential Corrosion and Degradation Mechanisms of Zircaloy Cladding on Spent Nuclear Fuel in a Tuff Repository*, UCID-20171, Lawrence Livermore National Laboratory, September 1984.
15. L. Young, *Anodic Oxide Film*, Academic Press, New York and London, pp. 257-258, 1961.
16. H. R. Peters, "Improved Characterization of Aqueous Corrosion Kinetics of Zircaloy-4," *Zirconium in the Nuclear Industry: Sixth International Symposium*, ASTM STP 824, D. G. Franklin and R. B. Adamson, Eds., American Society for Testing and Materials, pp. 507-518, 1984.