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Zinc-Zircaloy Interaction in Dry Storage Casks

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Zinc-Zircaloy Interaction in Dry Storage Casks

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ABSTRACT

Due to limited storage capacity in spent-fuel pools, some nuclear power plants are storing spent-fuel assemblies in inert-atmosphere dry casks until long-term geological depositories are available. VSC-24 is one such type of cask being used by utilities. During spent-fuel loading, the VSC-24 casks are submerged in the borated pool water and then dried and sealed. To mitigate contamination of the pool water and corrosion of the cask, a zinc-based primer coating, CarboZinc11, is applied to the cask structure, such as the fuel assembly sleeves and the cask shell. A series of laboratory tests was conducted to evaluate possible metallurgical interactions between zinc from the CarboZinc11 primer and the Zircaloy-4 cladding. The postulated transport mechanism of zinc is vaporization. If such interaction occurs during spent-fuel storage, performance of the Zircaloy-4 cladding as the primary barrier for fuel and fission products could be degraded.

The tests were designed to simulate realistic cask loading and storage conditions, including borated water immersion, vacuum drying, helium backfill, and elevated-temperature holds. Prototypical cladding and coating materials were used and the cladding was preoxidized to form a surface layer comparable to those on irradiated fuel rods at medium burnup. The test temperature was 300°C (which envelops the peak cladding temperature of 282°C at a realistic cask heat load of 12 kW) and the maximum hold time at temperature was 90 days. No zinc-Zircaloy interaction was found in any of the tests. These results differ from those of earlier tests conducted under less prototypical and generally more aggressive conditions. The major influence on the test results apparently was the oxide layer on the cladding specimens in the present tests. The oxide layer appears to be effective in blocking the migration of zinc vapor to the Zircaloy metal substrate. Because an oxide layer is always formed on fuel rod cladding from in-reactor service, the cladding would be protected as long as the oxide layer remains intact and adherent to the Zircaloy metal.

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ABBREVIATIONS

ANL	Argonne National Laboratory
EDX	energy-dispersive X-ray spectrometry
EOL	end of life
MSB	Multiassembly Sealed Basket
NIST	National Institute of Standards and Technology
PWR	pressurized water reactor
SEM	scanning electron microscope
TMI-1	Three Mile Island Unit 1
TREX	tube reduced extrusion
VSC	Ventilated Storage Cask

1 INTRODUCTION

Due to limited storage capacity in spent-fuel pools, some nuclear power plants are storing spent-fuel assemblies in inert-atmosphere dry casks, such as Pacific Sierra Nuclear Corporation's VSC-24 [Ref. 2], until long-term geological depositories are available. During spent-fuel loading, the VSC-24 casks are submerged in the borated pool water and then dried and sealed. To mitigate contamination of the pool water and corrosion of the cask, a zinc-based primer coating, CarboZinc11, is applied to the structures of the Multiassembly Sealed Basket (MSB) of the cask. The coated structure includes the fuel assembly sleeves and the MSB shell.

Zinc has a low melting point and an appreciable vapor pressure at cask drying and storage temperatures (≈282°C peak at a realistic cask heat load of 12 kW [Ref. 2] and ≈364°C peak at the maximum design heat load of 24 kW [Ref. 1]). It is conceivable that zinc may migrate to the fuel rods via a vapor-transport mechanism and interact with the Zircaloy-4 cladding in storage. In prior laboratory tests [Ref. 3] conducted by NIST to study the fundamental reaction kinetics, such vapor-phase transport occurred in their test apparatus and resulted in the formation of Zn-Zr intermetallics. The reactions caused a substantial degradation of the mechanical properties, i.e., strength and ductility, of the Zircaloy. However, because the NIST tests were conducted under simplified laboratory conditions significantly different from those of actual cask handling and storage and were generally more aggressive, the NIST findings may not be directly applicable to cask performance evaluation. Atypical conditions in these earlier tests include:

- The zinc source was high-purity zinc, not CarboZinc11 primer.
- Many of the specimens were machined pieces from extrusion stock, not cladding tubes.
- Most of the Zircaloy specimens had bare metal surfaces without the oxide layer expected on spent-fuel rods.
- For those specimens with an oxide layer, thickness and morphology of the oxide layer were not typical.
- Operations associated with cask loading, including exposure to borated water and vacuum drying, were not simulated.
- Spacing and areal ratio between the zinc source and Zircaloy specimen did not conform to the cask configuration.

Under these conditions, the NIST tests showed:

- Formation of small Zn_3Zr nodules on bare Zircaloy specimens after 90 days at 300°C.
- Formation of ZnZr and Zn_2Zr layers under the oxide layer of preoxidized specimens after 10 days at 350°C.
- Varying degrees of metallurgical interactions in all bare specimens after 10 days at temperatures ≥350°C.
- Reaction layer thickness generally greater than predicted on the basis of an activation energy of 140 J/mole derived from earlier tests at higher temperatures (650-700°C).

In the present work, conditions and materials more relevant to cask operations were incorporated. The objective was to determine the extent of interactions between zinc and Zircaloy-4 under these more realistic conditions.

2 DESCRIPTION OF PREVIOUS INVESTIGATIONS

NIST performed two series of laboratory tests to study the kinetics of Zn-Zircaloy interaction and the effects of such interaction on the mechanical properties of Zircaloy.

The first series was performed mostly at high temperatures (650 to 700°C) to determine the rate of layer growth, i.e., the Arrhenius rate equation, including activation energy. Because the test temperatures were above the zinc melting temperature (419°C), brass was used as the source of zinc. The data would then be used to predict reaction kinetics at lower temperatures germane to cask storage. However, in a test conducted at 350°C for 169 days in the same series, the reaction did not result in a uniform layer on the surface. Rather, it formed a large number of bead-like reaction products that covered almost the entire surface of the Zircaloy specimen to a thickness of ≈25 μm. The composition of the reacted material corresponded to Zn_3Zr. This thickness is much greater than predicted from extrapolation of the 650-700°C test results, and it suggested that the reaction mechanism at the lower temperature was significantly different from that prevailing between 650 and 700°C. More low-temperature exposure tests were therefore needed to understand the probable progression of reactions in casks during prolonged storage.

The lower-temperature tests were the main thrust for the second NIST series. The tests in the second series, documented in Ref. 2, were conducted in quartz ampoules mostly at temperatures from 300 to 400°C. Only two of the tests were conducted at the higher temperature of 650°C. The source of zinc was zinc metal, not brass. Two types of Zircaloy were used: machined parts from Zircaloy-4 tube reduced extrusion (TREX) stock, and Zircaloy-4 cladding tubes. Some of the tube specimens were preoxidized in pure oxygen to a nominal oxide thickness of 100 μm to simulate the oxide layer on fuel rods at end-of-life (EOL). Test durations of the second series of tests ranged from 10 to 103 days.

The test matrix and summary results for the second series are shown in Table 1. The major findings from these tests were:

- The reaction kinetic is strongly temperature-dependent in the range of 300 to 400°C. The kinetics may also be strongly dependent on other factors, such as the condition of the Zircaloy surface. At the low end of this temperature range, a few minute particles of Zn_3Zr were observed after the longest exposure time, but these observations were not sufficient to develop a credible model for the reaction rate at this temperature. At 350°C, significantly larger and more abundant nodules of Zn_3Zr were formed, but their sizes and distributions did not vary systematically with exposure time. This implied that the reaction at this temperature was sensitive to the detailed condition of the sample surface, as would be expected for a nucleation and growth process. However, at 400°C, the reaction was very different and occurred by a uniform reaction mechanism much more rapid than the nodular growth observed at the lower temperatures.

- The oxide coating on EOL Zircaloy-4 tubes was found to be effective in reducing the rate of reaction of zinc vapor with the underlying Zircaloy, even though the oxide showed numerous cracks that would have facilitated penetration by zinc vapor. The reaction

was much more rapid at or near regions where the oxide coating was removed, and the potential exists for penetration of the Zircaloy in such regions.

- Any prediction of the long-term behavior of Zircaloy-4 clad fuel rods in a storage cask that has been coated with zinc paint would have to be made on the basis of measurements or analysis of supply, transport, and redistribution of zinc within the cask. An intact coating of oxide on the fuel rods can significantly reduce the rate of reaction of the zinc vapor with the fuel rods, perhaps providing sufficient time for the zinc to move elsewhere in the container.

- C-bend and tensile tests showed significant reductions in strength and ductility of Zircaloy associated with exposure to zinc at elevated temperatures. These strength reductions could be correlated with the thickness of the intermetallic layer that formed. Ductility reductions due to exposure were related to the layer thickness in a more complex way. Unreacted Zircaloy always exhibited a fibrous fracture surface for all conditions of exposure to zinc. The intermetallic compounds that formed always exhibited a cleavage fracture surface.

Table 1. Summary Results of the Second Series of NIST Test [Ref. 3]

Temp. (°C)	Duration (d)	Zry Form	Tube OD (mm)	Oxide (micron)	Sample Number	Comments
300	10	Bare (TREX)	63.5	0	ZR9	No intermetallic detected
	30	Bare (TREX)	63.5	0	ZR13	No intermetallic detected
	90	Bare (TREX)	63.5	0	ZR5	Widely scattered 2 micron Zn3Zr nodules, 10% area
350	10	Bare (TREX)	63.5	0	ZR7	7 micron Zn3Zr nodules, near 100% area
	30	Bare (TREX)	63.5	0	ZR10	5 micron Zn3Zr nodules, 30% area
	90	Bare (TREX)	63.5	0	ZR12	Uniform Zn3Zr layer, 70-80 micron thick
350	90	Bare (tube tensile)	12.7	0	MT8	Nodular Zn3Zr, 15 micron thick on ID, 25 micron on OD
	90	Bare (tube tensile)	12.7	0	MT9	Layer, 100 micron on ID, 40 micron on OD
350	10	Oxidized tube	12.7	100		ZnZr and Zn2Zr layer under oxide in some region
	90	Oxidized tube	12.7	100		No intermetallic under oxide in any region
400	10	Bare (TREX)	63.5	0	ZR6	Near continuous 10 micron Zn3Zr/Zn2Zr nodules
	30	Bare (TREX)	63.5	0	ZR8	450 micron layer (outer 380 Zn6Zr; 70 Zn3Zr)
	90	Bare (TREX)	63.5	0	ZR11	520 micron layer (outer 280 Zn6Zr; 240 Zn3Zr)
400	90	Bare (tube tensile)	12.7	0	MT14	60 micron Zn3Zr layer on ID and 50 micron on OD
	103	Bare (tube tensile)	12.7	0	MT6	100 micron Zn3Zr layer on ID and 75 micron on OD
650	10	Oxidized tube	12.7	100		Flaky oxide, 5-20 micron intermetallic under oxide, 170 micron w/o oxide
	90	Oxidized tube	12.7	100		15 micron intermetallic under oxide

3 OBJECTIVES OF PRESENT STUDY

The NIST results indicate that 300°C appears to be the borderline temperature for discernible zinc-Zircaloy interaction in a reasonable period of time. The tests also showed that the condition of the Zircaloy surface, such as the oxide layer, may be significant in impeding the interaction, at least at temperatures ≥350°C. Several questions could not be answered by the NIST tests, which were fundamental kinetics studies under atypical in-cask conditions.

In the present study, more refined tests taking into consideration cask-specific details were conducted. The objective of the current study was to determine if zinc-zirconium intermetallics could form on oxide-coated Zircaloy-4 fuel rods exposed to CarboZinc11 under conditions representative of those inside the VSC-24 cask during actual use. The selected test temperature was 300°C for the present study as it envelops the peak cladding temperature of ≈282°C at the realistic cask heat load of 12 kW.To be representative of actual cask conditions to the extent possible, the present study included the following features:

- Prototypical materials (oxidized Zircaloy-4 cladding tubes and CarboZinc11-coated coupons).
- Test geometry simulating fuel rods configuration in the VSC-24 cask in terms of cladding-coating spacing and areal ratios.
- Test environment simulating the VSC-24 cask loading and storage, including borated water immersion, draining, vacuum drying, and elevated-temperature (300°C) holds of 2 hours (baseline), 45 days, or 90 days in a helium environment.

4 EXPERIMENTAL

4.1 Test Materials

4.1.1 Cladding Specimens

The test specimens were 38-mm-long sections of a Zircaloy-4 cladding tube procured from a commercial cladding vendor. With a tin content of 1.56 wt.%, outside diameter of 10.82 mm, and wall thickness of 0.79 mm, this tubing is representative of Zircaloy-4 cladding in medium-burnup (<≈45 GWd/MTU) 15 x 15 PWR rods currently in VSC-24 cask storage.

After their ends were sealed with Zircaloy plugs by electron-beam welding, cladding sections were oxidized to develop a surface oxide layer simulating that from in-reactor service. Due to practical considerations, the oxide on the specimens was formed in air, not in pressurized water or steam. After several trials, the conditions used to produce the specimens used in tests were finalized at 625°C for 23 hours. The oxidation was conducted in a heat-treatment furnace.

Figure 1 shows the cladding specimens after oxidation. The color of the oxide layer was light beige, consistent with results obtained previously by others [Refs. 4 and 5].

The resultant oxide layer was ≈20-35 μm thick, which compared reasonably well with that in medium-burnup PWR rods, ≈20-40 μm [Refs. 6and 7]. The morphology of the oxide layer also appeared to be comparable to that of an in-reactor oxide layer. Figure 2 shows the microstructure of the formed oxide layer in comparison with that in a TMI-1 rod at 50 GWd/MWU. Numerous, mostly circumferentially oriented, microvoids can be seen in both cases. When interlinked, these microvoids can lead to partial spallation of the oxide. However, because of apparent firm bonding between the oxide and the Zircaloy substrate, no spallation appears to have resulted in the exposure of bare metal.

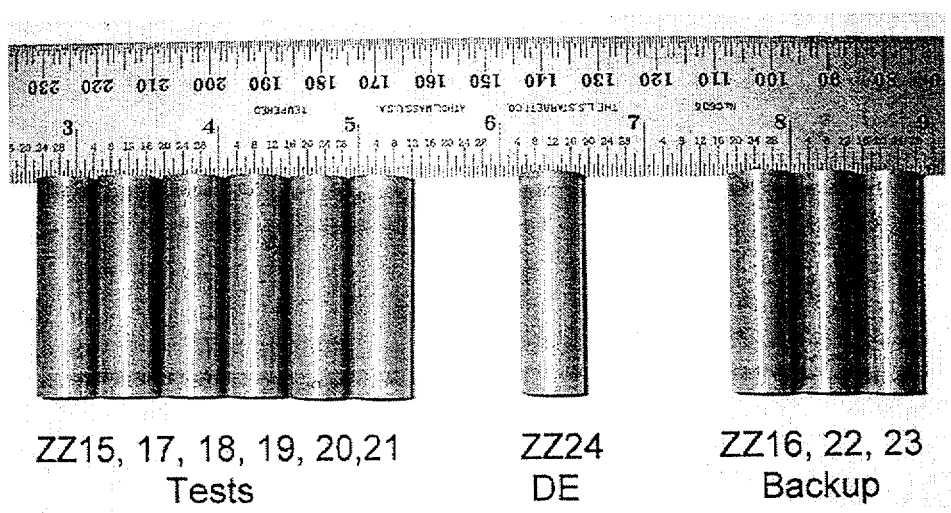
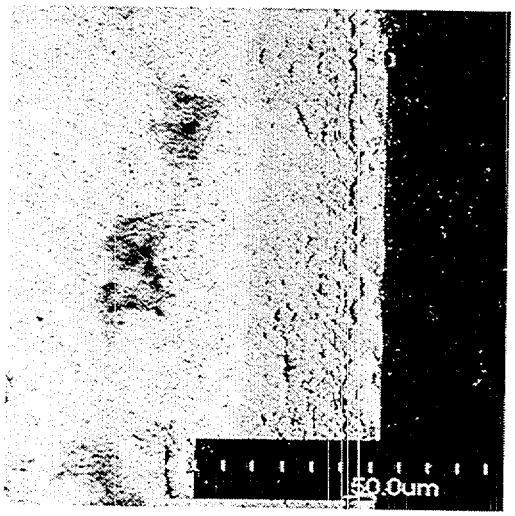
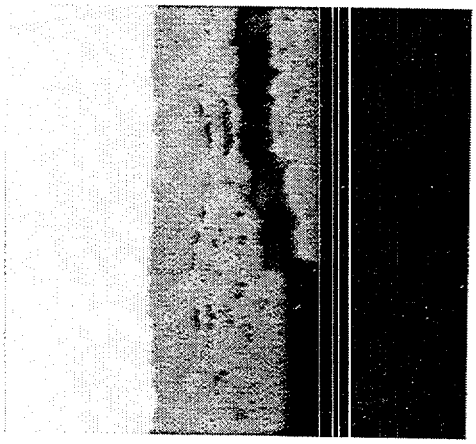


Fig. 1. Oxidized Zircaloy-4 cladding specimens in present study. Oxide color is beige.



2a



2b

Fig. 2. Cladding oxide layer on test specimens (2a, transversely mounted sample) and on irradiated TMI-1 cladding at ≈50 GWd/MTU (2b, longitudinally mounted sample). Numerous circumferentially oriented microvoids may contribute to partial spallation of layer. Bonding between oxide and Zircaloy substrate appears tight in both cases.

4.1.2 Coated Coupon

CarboZinc11, a zinc-base primer coated on 3-mm-thick carbon steel plates, was the source of zinc in the present tests. The coating was applied on the steel plates by the vendor of the primer. Color of the coating is gray.

The microstructure of the CarboZinc11 coating is shown in Fig. 3. The dried coating consisted of near-spherical particles of zinc of various sizes in a somewhat porous matrix of Si-O-Zn. Some of the zinc particles on the surface are only partially embedded in the matrix. Due to the uneven surfaces of the steel substrate and the coating, the layer has a substantial variation in thickness, from ≈50 to 100 μm. Overall zinc content is ≈85 wt.%, according to the vendor.

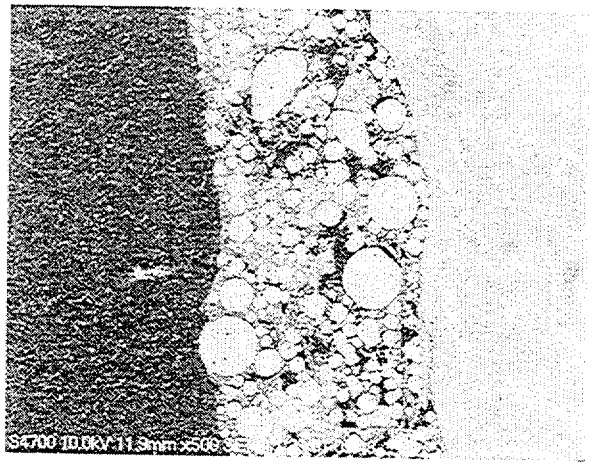


Fig. 3. Microstructure of CarboZinc11 coating on steel plate. Coating consists of near-spherical particles of zinc in a somewhat porous matrix of zinc, silicon, and oxygen. Thickness of coating ranged from ≈50 to 100 μm.

4.1.3 Test Apparatus

A series of four canister tests was performed in the present study. Each canister contained a specimen assembly consisting of two oxidized cladding specimens and a coated steel coupon arranged in the configuration shown in Fig. 4. The design provided coating-to-cladding spacing (3.4 mm) and areal ratio (0.3) typical of those for peripheral fuel rods adjacent to the coated fuel sleeves in the MSB of the VSC-24 cask. In some canisters, both sides of the coupon were coated, resulting in a coating/cladding areal ratio of 0.6. This condition constituted an overtest.

Arrangement of the test canisters is shown in Fig. 5. Three canisters were connected into a tree-like assembly with welded tubing; the fourth was attached to the system later after one of the canisters was discharged. Through the connecting tubing, the required environmental variables were administered to all three canisters. A valve in the system allowed the canisters to be shut off during the hold to prevent the zinc vapor from escaping. The required test temperature was achieved with a crucible furnace equipped with temperature feedback control. Temperature was monitored with thermocouples and recorded digitally.

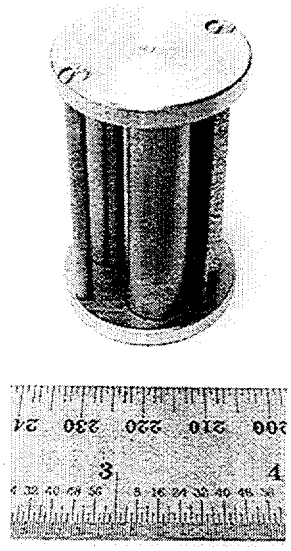


Fig. 4. Test specimen assembly consisting of two oxidized cladding tubes and a CarboZinc11-coated carbon steel coupon. All test hardware was made of Type 304 stainless steels.

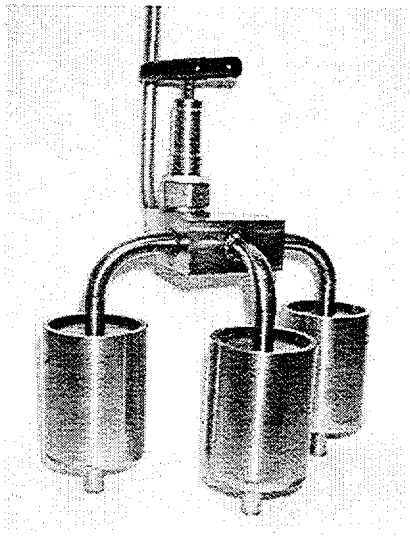


Fig. 5. Configuration of test canisters before exposure tests in furnace. A shut-off valve, located in hot zone of furnace, prevented loss of zinc vapor. Openings at bottoms of canisters were capped after draining of borated water.

4.1.4 Test Conditions and Conduct

The exposure tests were designed to simulate both cask loading and storage. The simulated loading sequences consisted of:

- Immersion in borated water (H_3BO_3 solution with boron content of ≈2800 wppm and a pH of ≈5.1) at 65°C for 5.5 hours.
- Bake-out at 95°C for 80.5 hours after draining.
- Bake-out at 300°C for 12 hours with periodic evacuation to simulate vacuum drying.
- Backfilling with high-purity helium to 1 atm at 300°C.

Following the simulated loading operations, the canisters were subject to elevated-temperature holds with durations of 2 hours (baseline), 45 days, or 90 days. The hold temperature was 300°C and the atmosphere was helium for all specimens. Heating was isothermal, i.e., with the cladding specimens and the coated coupon at the same temperature. (This condition is not prototypical for the MSB, in which both radial and axial temperature gradients exist.) Table 2 summarizes the test conditions.

The exposure tests began with Canisters 1, 2, and 3 on December 15, 2000. Canister 3 was discharged on December 20, after the simulated loading sequence and 2 hour hold. Canister 2 was discharged on February 3, 2001 after completing the 45 day hold. During the Canister 2 removal outage, Canister 4 was attached to the test assembly and the exposure resumed with Canisters 1 and 4. On March 22, 2001, Canisters 1 and 4 were discharged after accruing 90 and 45 days of exposure, respectively.

The hold temperature of 300°C was maintained to within ±1°C throughout the tests.

Table 2. Summary of test conditions

Canister No.	Exposure Conditions	Hold Temp. (°C)	Coating/Cladding Areal Ratio
3	Loading + 2 h hold	300	0.6
2	Loading + 45 d hold	300	0.6
1	Loading + 90 d hold	300	0.6
4	Loading + 45 d hold	300	0.3

5 EXPERIMENTAL RESULTS

Microstructures of the cladding specimens and the primer-coated coupons before and after the exposure tests were characterized by scanning-electron microscopy. All samples were mounted transversely for examination. The emphasis for the posttest characterization of the coupons was coating thickness and formation of reaction layers with boron (from the boric acid immersion). Emphasis for the cladding specimen examination was to detect zinc and characterize any reaction phases.

The field-emission scanning electron microscope (SEM) had an energy-dispersive X-ray (EDX) spectral analysis capability for identifying elements. The finely focused electron beam from the field emission gun resulted in a small interaction volume (≈0.2-μm diameter at the applied voltage of 5 keV) and consequently high spatial resolution. To provide the required electric conductivity, the samples were coated with a thin layer of carbon.

5.1 Pretest Characterization

EDX analysis was performed on an oxidized cladding sample to establish the zinc-free baseline. The results are shown in Fig. 6 for two representative spots: one near the surface of the oxide and another in the Zircaloy just inside the oxide layer. The spectra showed predominantly zirconium and oxygen and no signs of zinc (L peak at 1.01 keV). As expected, the oxygen peak in the oxide layer is more prominent than that in the Zircaloy substrate adjacent to the oxide. In both spectra, the carbon peak in the spectra was from the coating and therefore an artifact. Qualitative EDX analyses at other locations of the sample showed the same results.

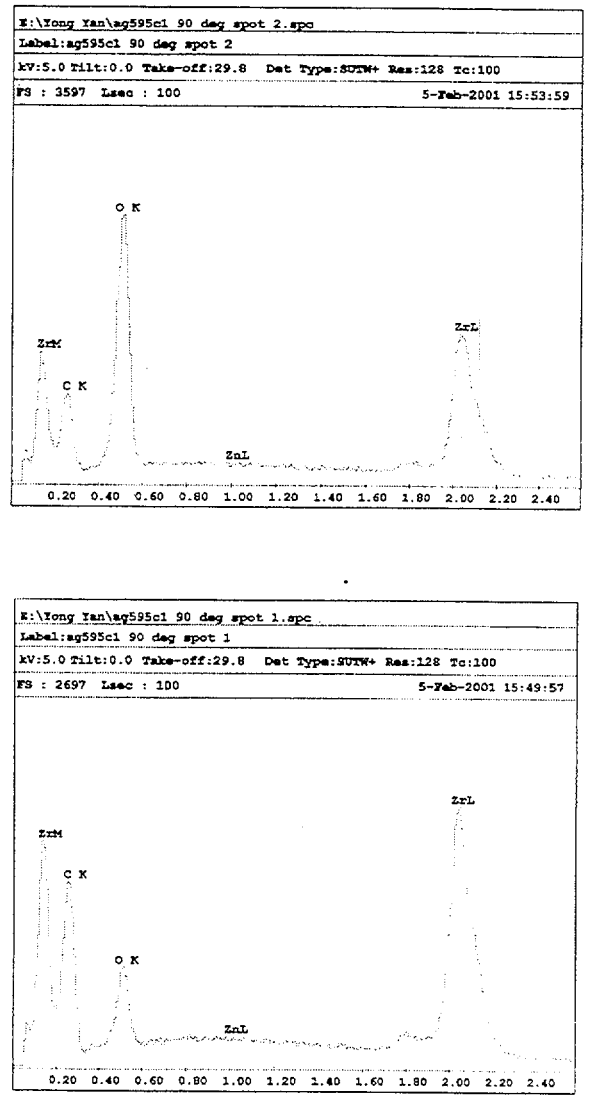


Fig. 6. Pretest EDX spectrum used to establish zinc-free baseline. Spot locations were (top) near the oxide layer surface and (bottom) in Zircaloy cladding just inside oxide layer. Carbon peak is an artifact from carbon coating.

5.2 Posttest Characterization

5.2.1 After 90-day Exposure

The specimens from Canister No. 1, with the longest elevated-temperature exposure (90 days) represent the worst case among all the test specimens. The specimen assembly removed from the canister showed no noticeable changes in cladding specimen appearance, in either color or finish. Coating appearance was also not different from that before the test. Figure 7 shows the specimen assembly after removal from the test canister.

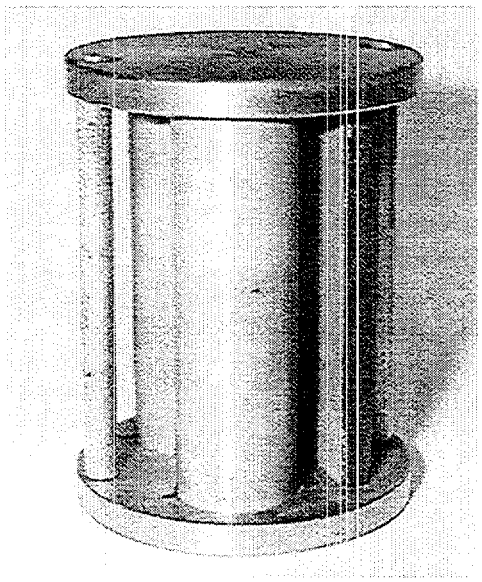


Fig. 7. Specimen assembly after 90-day exposure; appearance is not noticeably different from before the test.

A transverse metallographic cross section near the axial midplane of a cladding specimen was prepared. The condition of the cladding is shown in Fig. 8. There was no evidence of second-phase formation, such as intermetallic nodules or layers, that would indicate zinc-Zircaloy interaction. Indeed, the morphology of the oxide layer and the cladding/oxide interface was essentially unchanged from that before the test. Thickness of the oxide layer was also virtually the same, indicating no further oxidation during the test.

Multiple locations on the 90-day cladding sample were analyzed by SEM-EDX to detect zinc. Data for the three locations labeled 1, 2, and 3 in Fig. 8 are shown in Fig. 9. Compared to the pretest spectrum shown in Fig. 6 for the nonexposed control, the results are virtually identical.

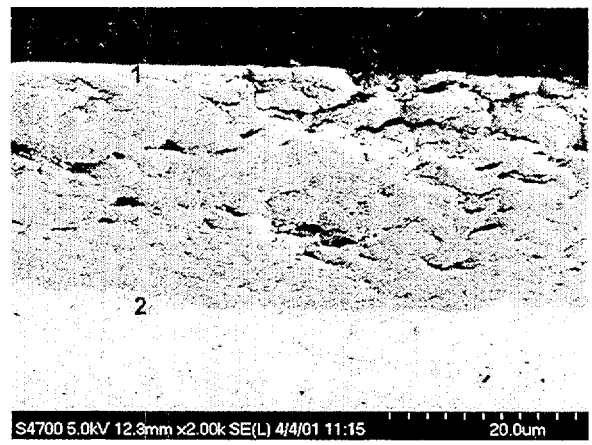


Fig. 8. Microstructure of cladding specimen after 90-day exposure. There is no evidence of zinc-Zircaloy interaction, and condition of oxide layer and cladding is comparable to that of the nonexposed control (see Fig. 2a). Three numbered locations are where EDX were performed.

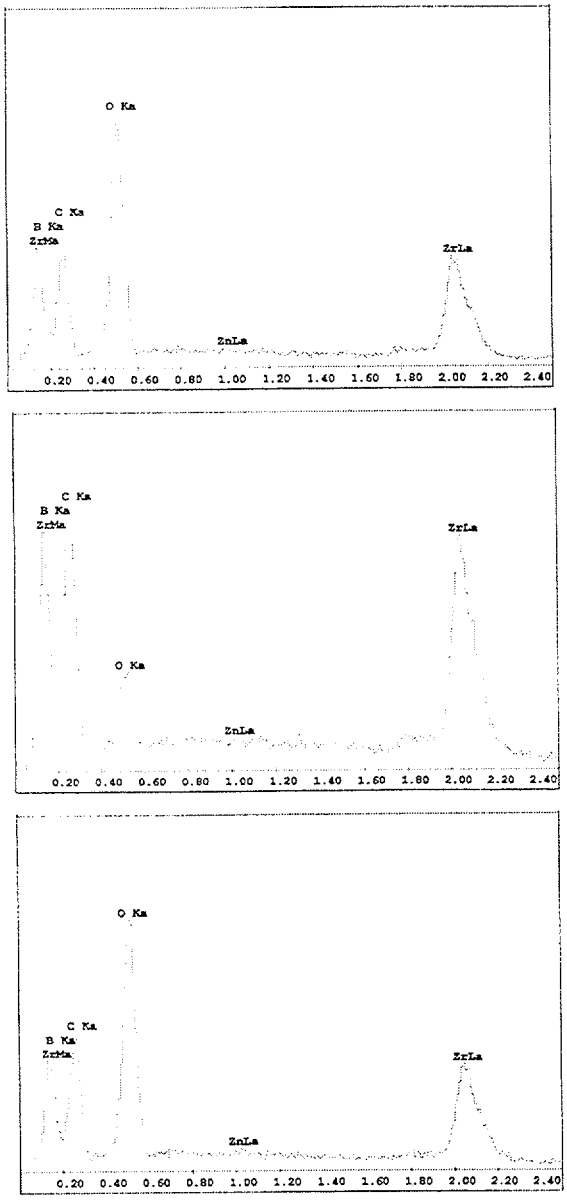


Fig. 9. Posttest EDX results for Spots 1, 2, 3 in Fig. 8 for 90-day cladding; no discernible zinc is seen in any of the three locations.

The condition of the CarboZinc11 coating after the 90-day exposure is illustrated in Fig. 10. Its thickness and morphology are also unchanged from before the test, indicating no significant vaporization during the test. Without a sink that would remove zinc from the vapor phase, such as from extensive Zn-Zr interaction, this outcome is to be expected because vaporization would effectively cease in the sealed canister once the saturation vapor pressure is attained at 300°C. The near-perfect spherical shape of the partially exposed zinc particles is further evidence that vaporization during the test was minimal. (If vaporization was significant, one would expect thinning of the exposed side, resulting in an oblong contour.)

The partially exposed zinc particles on the surface were examined at high magnification and analyzed by EDX to determine whether there is a surface layer from reaction with the boric acid. (Such a reaction layer could have retarded zinc vaporization during the test.) No discernible reaction layers could be found, either visually or by EDX. Figure 11 shows a cross section of one such partially exposed zinc particle.

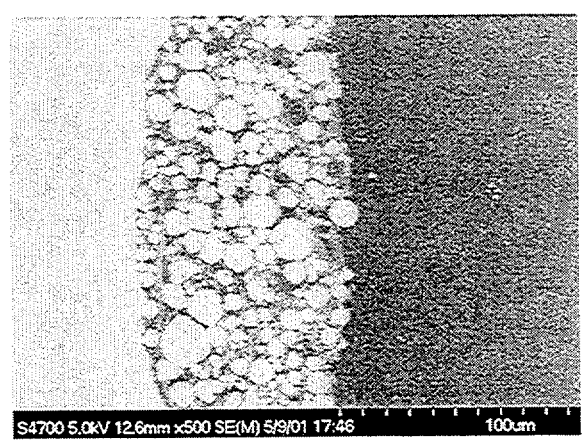


Fig. 10. CarboZinc11 coating after 90-day exposure. Thickness and morphology are essentially the same as before the test, indicating minimal vaporization; spherical shape of partially exposed zinc particles on surface is another indication that vaporization was minimal.

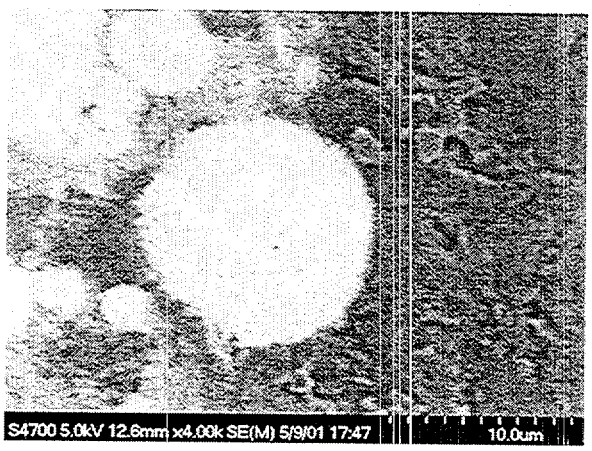


Fig. 11. Exposed zinc particle in CarboZinc11 coating. No surface layer from reaction with boric acid could be identified; such a layer could have retarded zinc vaporization during the tests.

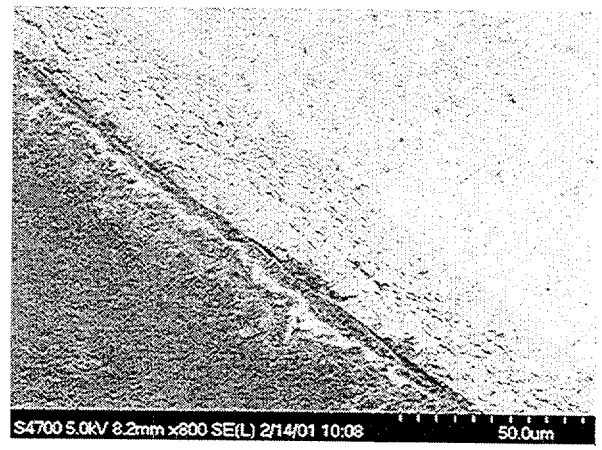
5.2.2 After 45-day Exposure

Two canisters were exposed for 45 days, one with a coating-to-cladding surface ratio of 0.3 (Canister 4) and the other with a ratio of 0.6 (Canister 2). There was no apparent zinc-Zircaloy interaction in either case.

Figure 12 shows the microstructures of the cladding specimens from the two canisters. There were no secondary phases that would indicate zinc-Zircaloy interactions. Multiple locations were examined by EDX and none show any zinc.

Microstructures of the CarboZinc11 coating after the 45-day exposures are shown in Fig. 13. Judging from the thickness and morphology of the exposed surface, no substantial vaporization occurred during the exposure.

The CarboZinc11 coating on the back of the coupon in Canister 4 was removed by scraping before the test. After the test, this exposed surface showed noticeable rust, apparently due to reaction with the mildly acidic borated water during the immersion. A comparison of uncoated and coated surfaces, illustrating the effectiveness of CarboZinc11, is shown in Fig. 14.



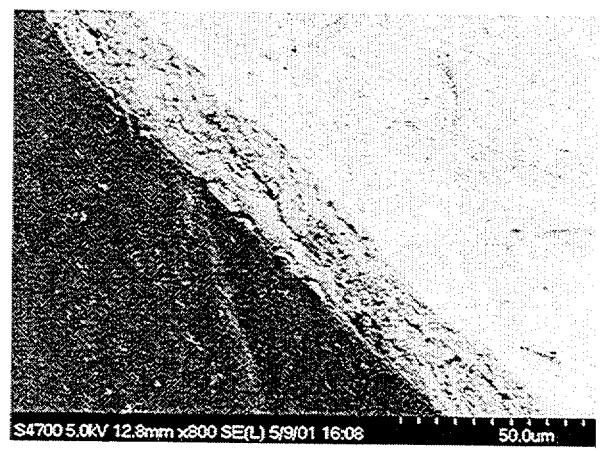


Fig. 12. Microstructures of cladding and oxide layer after 45-day exposure to CarboZinc11. Coating/cladding areal ratio was 0.6 (top) and 0.3 (bottom); no apparent Zn-Zircaloy interaction is seen in either specimen.

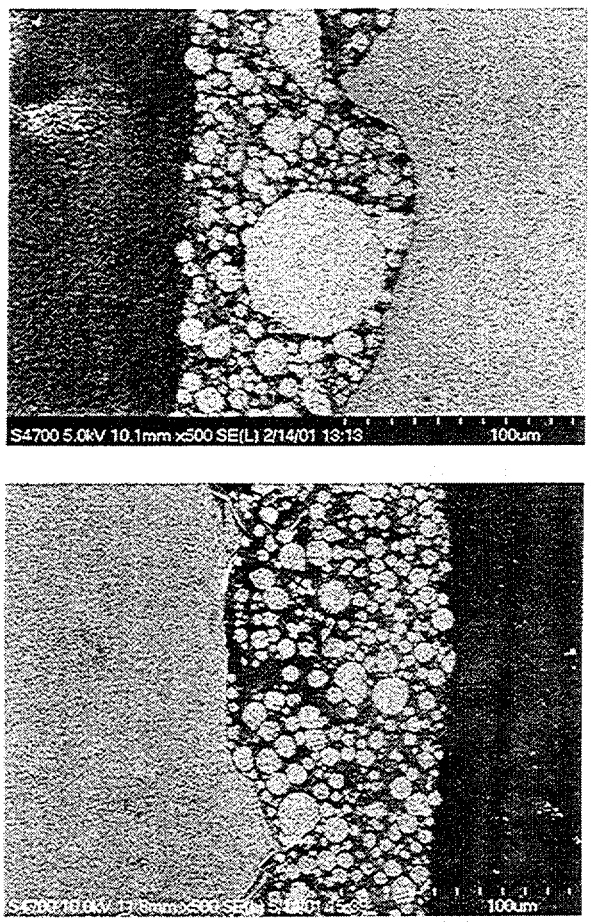


Fig. 13. CarboZinc11 coating after 45-day exposure, from Canister 2 (top) and Canister 4 (bottom). No significant vaporization occurred in either case.

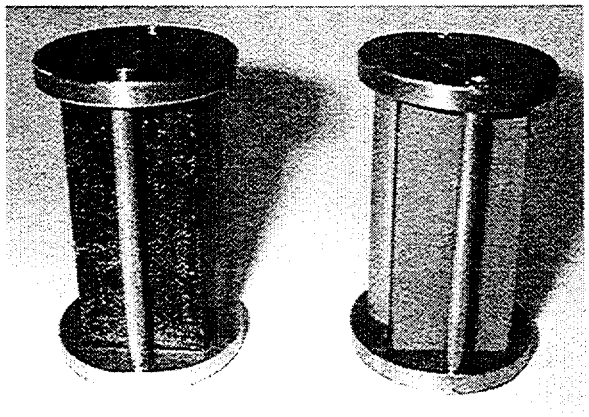


Fig. 14. Effectiveness of CarboZinc11 coating in protecting carbon steel surface; substantial rust on uncoated surface (left, from Canister 4) and free of rust on coated surface (right, from Canister 1).

5.2.3 After 2-hour Exposure

The results from the 2-hour exposure test were essentially the same as from the longer-exposure tests, i.e., showing no detectable zinc-Zircaloy interaction. Conditions of the cladding and the CarboZinc11 coating after the test are shown in Fig. 15. As before, SEM-EDX analyses did not reveal detectable zinc in the cladding.

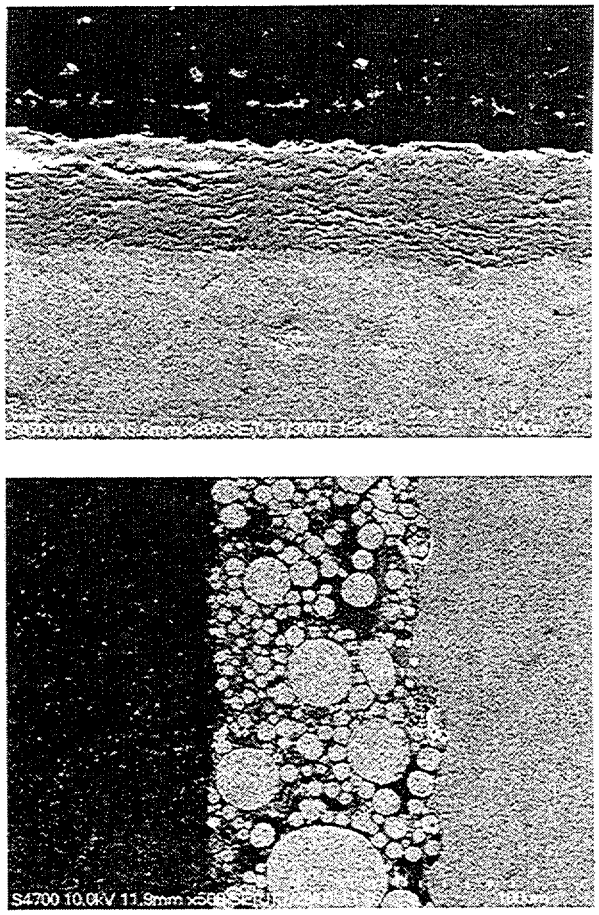


Fig. 15. Cladding (top) and coated coupon (bottom) after 2-hour exposure; no discernible zinc-Zircaloy interaction is visible.

6 DISCUSSION

The benign results from the present work contrast significantly with those of the NIST tests, which showed Zn-Zr interaction, albeit incipient, on a bare specimen at 300°C after 90 days. There were a number of differences in the test design and conduct; their effects on test outcomes are discussed below.

1. Pure Zinc vs. CarboZinc11

   Pure zinc was used in the second series of the NIST tests, whereas CarboZinc11 was used in the present tests. Both tests used small sealed test volumes – quartz ampoules for NIST and stainless steels canister for ANL – under isothermal conditions.

   Because the CarboZinc11 coating invariably had exposed zinc particles on the surface, it is believed that the vapor pressures in both tests were that of the saturation vapor of zinc at the 300°C test temperature. Without sinks that would eliminate zinc from the system (such as extensive zinc-Zircaloy reactions), the vapor pressure would remain constant throughout the test. Once the saturation vapor was attained, further evaporation would effectively cease in the sealed test volume. Therefore, the difference in the form of zinc most likely played no role in affecting the reaction kinetics in the tests.

2. Coating/Cladding Spacing and Areal Ratio

   In the NIST tests, the Zircaloy test specimen was placed at the top of the quartz ampoule and the zinc metal source at the bottom. The two were separated by a quartz tubing spacer. This arrangement renders less geometric control than in the ANL tests.

   However, this difference likely also played no significant role in affecting the test outcome. As indicated before, during the exposure, the sealed and isothermal test volumes in both the NIST and ANL tests were filled with zinc vapor at the saturation pressure. Spacing or area ratio would have no impact on this vapor pressure.

   In the ANL tests, Canisters 2 and 4 had a factor of 2 difference in surface area and zinc inventory, but the results of the two tests were virtually identical.

   One notable difference between the laboratory tests and actual casks is that the laboratory tests were isothermal, whereas the actual casks have substantial radial and axial temperature gradients. Thus, in casks, the zinc vapor may condense at cold spots (e.g., the ends of cask or the outer periphery) and be effectively removed from the interaction. In this respect, the isothermal laboratory tests were more aggressive than the in-cask situation.

3. Simulated Cask Loading Procedure (Borated Water Immersion and Vacuum Drying)

   In the ANL tests, the specimens and the CarboZinc11 coating were immersed in borated water (an aqueous solution of boric acid with a pH of 5.1) for 5.5 hours at 65°C before exposure. If the boric acid reacted with the CarboZinc11 and passivated the coating surface, it could have retarded the vaporization of zinc

during the elevated-temperature hold. However, as shown in Fig. 11 and in extensive EDX examination, no such layer could be found.

In the ANL tests, the test volumes were evacuated several times at 300°C during the simulated vacuum drying operation. The evacuation undoubtedly removed some of the zinc vapor from the system, but the amount removed was probably modest because the vapor pressure of zinc is only ≈0.16 Pa at 300°C. Because exhaustion of zinc was not an issue in the ANL tests, the vacuum drying operation probably did not affect the test results.

4. Cladding Surface Condition

By far the most important factor that affected the test outcome was the oxide layer on Zircaloy tubing in the present tests. This layer was evidently protective, and some of this effect could be seen in the higher-temperature NIST tests [Ref. 3].

The oxide layer on the few NIST samples that were preoxidized was relatively thick (≈100 μm, to simulate end-of-life conditions in fuel rods) and contained radial cracks most likely from thermal contraction during cool-down at the end of oxidation. Such radial cracks were not seen in the ANL samples with thinner layers. These radial cracks may not occur in irradiated fuel rods either, because the in-reactor oxide is formed gradually over an extended period of time. In the NIST samples, where the oxide was intact and adherent, zinc-Zircaloy interaction was nonexistent or minimal; where the oxide layer was cracked or not adherent, intermetallic formation was more extensive.

For the cladding to be protected, the oxide layer on irradiated fuel rods must remain intact during cask loading and storage. As illustrated in Fig. 2b for a TMI-1 rod, and seen in other examinations that have been performed, it appears that although the in-reactor oxide layer may spall at mid-thickness, the remaining layer would stay intact and adherent to the cladding. However, this condition is difficult, if not impossible, to verify universally. Further study would be required to fully address this issue.

5. Temperature

The scope of the present study limited the tests to one temperature – 300°C. This temperature envelops the predicted peak cladding temperature of ≈282°C in a VSC-24 cask with a realistic heat load of 12 kW [Ref. 2]. The results from the present study would not be conservative, however, for the VSC-24 cask at its design heat load of 24 kW. At the design heat load, the temperature of the MSB sleeve could be as high as 364°C during normal long-term storage [Ref. 1] and that of the cladding would be even higher. Therefore, the results and conclusions obtained in the present study may not be applicable for those higher-temperature conditions.

7 CONCLUSIONS

A zinc-based primer, CarboZinc11, is being used as a protective coating for the exposed steel surfaces inside VSC-24 dry storage casks. A series of laboratory tests was conducted to evaluate possible metallurgical interactions between zinc and the Zircaloy-4 cladding during spent-fuel storage. The postulated migration path of zinc to the cladding is vapor transport due to the relative high vapor pressure of zinc at the cask temperature. Tests in the present study were performed with conditions simulating cask loading and storage, including borated water immersion, vacuum drying, helium backfill, and elevated-temperature holds. The cladding specimens were preoxidized before the tests to form an oxide layer comparable to that on spent fuel rods. Peak test temperature was 300°C and maximum hold time at temperature was 90 days. No zinc-Zircaloy interaction was detected in any of the tests. These results differ from those from an earlier series of tests conducted by NIST with bare Zircaloy materials that showed metallurgical interaction under identical conditions. It is believed that the oxide layer in the present tests played an important role in blocking the zinc vapor from the Zircaloy-4 material. Because an oxide layer is always formed on fuel rod cladding during in-reactor service, the cladding would be protected as long as the oxide layer remains intact and adherent to the Zircaloy metal.

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10. SUPPLEMENTARY NOTES

D.N. Kalinousky, NRC Project Manager

11. ABSTRACT *(200 words or less)*

Due to limited storage capacity in spent-fuel pools, some nuclear power plants are storing spent-fuel assemblies in inert-atmosphere dry casks until long-term geological depositories are available. VSC-24 is one such type of cask being used by utilities. During spent-fuel loading, the VSC-24 casks are submerged in the borated pool water and then dried and sealed. To mitigate contamination of the pool water and corrosion of the cask, a zinc-based primer coating, CarboZinc11, is applied to the cask structure, such as the fuel assembly sleeves and the cask shell. A series of laboratory tests was conducted to evaluate possible metallurgical interactions between zinc from the CarboZinc11 primer and the Zircaloy-4 cladding. The postulated transport mechanism of zinc is vaporization. If such interaction occurs during spent-fuel storage, performance of the Zircaloy-4 cladding as the primary barrier for fuel and fission products could be degraded.

The tests were designed to simulate realistic cask loading and storage conditions, including borated water immersion, vacuum drying, helium backfill, and elevated-temperature holds. Prototypical cladding and coating materials were used and the cladding was preoxidized to form a surface layer comparable to those on irradiated fuel rods at medium burnup. The test temperature was 300ÇC (which envelops the peak cladding temperature of 282ÇC at a realistic cask heat load of 12 kW) and the maximum hold time at temperature was 90 days. No zinc-Zircaloy interaction was found in any of the tests. These results differ from those of earlier tests conducted under less prototypical and generally more aggressive conditions. The major influence on the test results apparently was the oxide layer on the cladding specimens in the present tests. The oxide layer appears to be effective in blocking the migration of zinc vapor to the Zircaloy metal substrate. Because an oxide layer is always formed on fuel rod cladding from in-reactor service, the cladding would be protected as long as the oxide layer remains intact and adherent to the Zircaloy metal.

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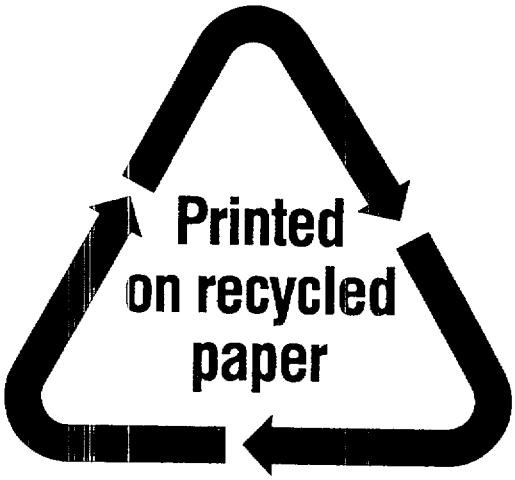

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