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In the Matter of
Public Service Electric and Gas Company, et al.
(Salem Nuclear Generating Station, Unit 1)
Docket No. 50-272

Gentlemen:

In order to minimize or eliminate the need for an <u>in camera</u> session with regard to the Exxon Nuclear Company's proprietary report, Fuel Storage Racks Corrosion Program, XN-NS-TP-009, I am transmitting herewith a non-proprietary version of that document to the Board and parties.

Sincerely,

Mark J. Wetterhahn

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Counsel for the Licensee

cc: Chairman, Atomic Safety and
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XN-NS-TP-009/NP

RELATED CORRESPONDENCE

DOCKETED USNRC APR 26 1979 Office of the Secretary Docketing & Service Section

FUEL STORAGE RACKS CORROSION PROGRAM, BORAL - STAINLESS STEEL

(NON-PROPRIETARY VERSION)

MARCH 1979

GR-005

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ABSTRACT

Exxon Nuclear Company, Inc. has conducted a Boral*-Stainless Steel Corrosion Program during the past 18 months to establish additional performance information for use of Boral plates in spent fuel storage applications. The program consisted of a detailed review of related literature, an evaluation of test programs conducted by others, and additional corrosion tests performed at Exxon Nuclear facilities.

The objective of the Exxon Nuclear test program was to obtain corrosion data for Boral-304 stainless steel test specimens in simulated PWR fuel pool environments so that reliable predictions could be made of what physical changes would occur in a defective, i.e., unsealed spent fuel storage cell after a 40-year exposure.

The Exxon Nuclear tests indicate that storage cells, containing a leak simulating hole, will sustain aluminum corrosion at a rate which can be expected to consume of the aluminum in the Boral core after a 40-year exposure.

Should Boral plates be exposed to a typical PWR pool environment, the material is subjected to pitting, edge attack, and internal gas pressurization; but no effect on criticality safety is expected over the lifetime of storage cells due to dislodgement of B_4C particles.

* The Boral test samples discussed in this report are a neutron absorbing, shielding material manufactured by the Brooks and Perkins Company. The Boral specimens are a composite material consisting of boron carbide evenly dispersed within a matrix of aluminum and clad with aluminum.

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1.0 INTRODUCTION

Prior to designing racks utilizing stainless steel clad Boral plates in PWR pool environments, Exxon Nuclear initiated, (during 1976 and early 1977), a review of applicable material corrosion literature and conducted analyses of test results performed by others.

Exxon Nuclear's review of the related literature*, and performance of Boral in similar environments, indicated that there should be no adverse effect on nuclear safety analyses of storage racks in a PWR pool environment. To provide further assurance of satisfactory material performance, Exxon Nuclear initiated a test program in February, 1977 to evaluate Boral clad in stainless steel 304 specimens in environments simulating utilization in Exxon Nuclear PWR storage rack applications.

* List of appropriate material contained in Reference section of this report.

2.0 TEST PROGRAM DESCRIPTION

2.1 SPECIMEN DESCRIPTION

Exxon Nuclear's test program placed emphasis on investigation of Boral utilized in conditions typical of expected storage cells and PWR pool water environments. Consequently, storage cell component sections were fabricated which resembled the larger, full-size storage cells. Specifically, these reduced-size storage cell specimens consisted of inner and outer stainless steel 304 shrouds into which four (4) Boral plates were inserted. The complete assembly was sealed welded, resulting in 6" high x 6" wide test specimens. Each completed cell specimen was made to simulate a leaking condition by drilling 1/16-inch holes as described in Appendix A.

In order to separately observe and measure various corrosion and material properties during the test, additional test specimens were utilized. These additional specimens consisted of 2" x 2" coupons made as follows:

1) Open-edge Boral/stainless steel composite;

2) Sealed-edge Boral/stainless steel composites with a leak simulating hole; and,

3) Unencapsulated Boral coupons.

2.2 ENVIRONMENT DESCRIPTION

Insulated nine (9) gallon polyethylene tanks, with fitted covers, were used for the plain Boral and open-edged Boral-stainless specimens. Thirty (30) gallon tanks of the same construction were used for the closed-edge tests. Each tank was fitted with a stainless immersion heater and stirring mixer, which were affixed through openings in the tank covers.

A stainless steel screen was used to hold the specimens off the bottom of the tanks and permit circulation of the environment on all sides. In order to isolate the plain Boral specimens from the stainless steel screen, a pedestal was fashioned from phenolic plastic. The open-edged composite samples, a 2" x 2" Boral piece sandwiched between two 2" x 2" stainless steel pieces, were held together with four (4) Met-clip springs, one along each edge. These were placed on the stainless screens so that the clips held the specimens in a horizontal position over the screen.

The initial environment in each tank was deionized water with a pH of 5.85 and a conductivity of 0.75 μ mho/cm. Boric acid (H_3BO_3) and lithium hydroxide (LiOH H_2O) additions were made to produce the following:

Environment A) Deionized water plus 13.3 g/l Boric Acid (resulting in 2300 ppm Boron at 150°F).

Environment B) Deionized water, 13.3 g/l Boric Acid, 0.0121 g/l lithium hydroxide

Environment C) Deionized water plus 0.0121 g/l lithium hydroxide

The specimens, were immersed in each environment on July 1, 1977. The initial temperature and pH of each environment were measured as follows:

Environment	pH	Temperature, °F
1	5.20	146.4
2	5.53	147.2
3	9.15	153.4

The temperature and pH were measured daily. The temperature showed some fluctuations and variacs were installed in order to gain better temperature control. The pH in the borated solutions, 1 and 2, remained constant but in the alkaline tank, C, it dropped into the 7 range within days. In order to keep the solution pH in the alkaline range, additional additions of lithium hydroxide were made.

2.3 INITIAL MEASUREMENTS

Appendix A of this report contains descriptions of all Boral and stainless steel specimens utilized for the test program. The initial measurements and cleaning programs are also provided in Appendix A.

3.0 SUMMARY

No corrosion, pitting, nor stress-corrosion cracking was observed on any of the stainless steel coupons, or storage cell specimens used in this study. The austenitic stainless steel can be expected to withstand exposure to borated fuel pool environments for the projected forty-year life of spent fuel racks. Similarly, without a leak path through the stainless steel liners, the interior Boral plates would not be subject to degradation as a result of aqueous corrosion. In the situation of a leak path through the stainless liners which permits the interior space to fill with the pool environments, the results of the 2 month, 6 month, and 12 month exposure studies, show that Boral is subject to general corrosion, pitting and edge attack, and clad deformation due to internal gas pressurization. To various degrees, the severity of each of these corrosion effects depends on the particular environment chemistry and the specific geometry of the exposed materials. Based on comparisons between the four (4) specimen types and the three (3) environments used in this study, the following summary can be drawn concerning the corrosion resistance of Boral and its suitability for use when exposed in stainless lined storage cells to borated environments.

The general corrosion rate, as determined by weight gain measurements,

When all the storage cell specimen data are examined on a semi-log plot, the amount of aluminum consumed in conversion to oxide after a 40-year exposure, is: percent for the low pH and   percent for the higher pH environments.

The weight gains were lowest for the storage cell specimens in each of the three (3) environments, followed in general by the plain, open-edged, and edge-sealed specimens. The weight gains, measured for the plain and open-edged specimens, were nearly identical to each other in the three (3) environments. This similarly indicates that galvanic coupling between the stainless steel in the open-edged specimens does not accelerate general corrosion in the Boral. In all three (3) environments, the edge-sealed specimens showed the greatest weight gain.

Similar considerations apply to edge attack of the Boral. However, the depth of edge attack did not increase significantly between the

6 and 12 month exposure. The deepest edge penetration, 0.028", was measured on the open-edged specimen in the low pH environment. No measurable edge attack was observed in the vicinity of the leak simulating hole in the Boral plates of the storage cell specimens.

Gas generation, due to corrosion of the aluminum in Boral, has been observed in the edge-sealed specimens and the storage cell specimens. This gas has been observed to bubble from the upper hole in each of the storage cells. In several of the specimens removed after 12 months, bulges were observed between the aluminum cladding and the B_4C aluminum core.

The occasional unbonded layers of the Boral matrix occurred randomly and were observed in concentrated areas of very small B_4C particles (i.e., $\geq$150 mesh). It has been determined that the Boral specimens provided by Brooks and Perkins for the ENC corrosion test program contained a much higher concentration of small B_4C particles than utilized for production Boral plates. Accordingly, it is possible that the small bulges observed on the sealed specimens may not occur in finished plates where improved B_4C and aluminum bonding result with larger B_4C particles.

The occasional lack of bonding between B_4C and aluminum particles also allows a small amount of water to enter the inner portions of the bulged specimens. Normally, water does not penetrate into well-bonded Boral plates and no internal corrosion can occur.

The small bulges have not been reported or observed in prior related corrosion test programs. They appear to be a self-limiting phenomenon, where the gaseous corrosion product both causes the bulge and displaces the water causing the corrosion. An inspection of both the aluminum cladding and inner Boral matrix demonstrates that no clad pitting or deterioration of the inner face of cladding and Boral material occurred near the bulged areas. Consequently should random small bulges occur, any dislodgement of B_4C particles will be of no significance on neutron shielding or attenuation properties.

4.0 RESULTS

On June 30, 1978, after a nominal 12-month exposure, the remaining three (3) plain Boral and three open-edged Boral-stainless composite specimens, were removed from the three (3) heated tanks. On August 10, 1978, the edge-sealed, and storage cell specimens, were removed from their environments. These twelve (12) samples were subjected to visual, metallographic, weight gain, and pit depth measurement analyses.

This section of the report places emphasis on the detailed results obtained from the storage cell specimens. Appendix B presents additional test results for other specimens and contains most referenced tables and figures for information presented in this section. Table 4.1 provides specimen identification numbers and exact lengths of exposure for each of the twelve (12) specimens evaluated during the final period.

4.1 Internal Environment Of Edge-Sealed And Storage Cell Specimens

The pH of the solution, within the edge-sealed and storage cell specimens, was measured using indicator paper for the former, and a Beckmann pH meter for the latter. Approximately 2.5 grams of solution was contained in the edge-sealed specimens and 39 grams in the cell specimens.

In Table 4.2 is a summary of the interior pH of the edge-sealed and cell specimens for the 2-, 6-, and 12-month exposures.

For the high pH lithium environment, the interior pH consistently shows a decrease in pH toward a neutral value for all exposure times. A similar trend toward a more neutral pH is exhibited for the acidic environments for exposures up to 6-months. After 12-months, the interior pH is the same as the bulk solution or, slightly more acidic.

4.2 Visual Appearance

The storage cell specimens were disassembled and cut open to separate the Boral plates from the stainless liners. A visual examination of each Boral piece was conducted using a low power stereo-microscope. The following observations were noted:

Storage Cell Specimen #3 (S.C.S.-3)

Surfaces were generally metallic in coloration. Extra corrosion products, and some pitting, were seen on the faces and along the edges where the leak simulating holes were drilled through the stainless liners.

Storage Cell Specimen #6 (S.C.S.-6)

Specimens are darker than SCS-3. Pitting is much less. Rust existed along edges where holes were drilled. Bulges were observed in the dimple area of plate S.C.S.-6(1), on both the outside and inside.

Storage Cell Specimen #9 (S.C.S.-9)

Specimens were white in coloration with rust colored deposits along the edges where holes were drilled. B_4C stringers were evident, but no pitting. Plate S.C.S.-9(4) had a 1-1/4" pure aluminum strip on one short edge.

4.3 Weight Gain

After the visual analysis, the appropriate Boral plate specimens were weighed, oven-dried, and reweighed in order to determine the amount of absorbed moisture in the core and the change in weight due to exterior and interior corrosion. The specimens were dried in stages in an air-circulating oven for two (2) hours at 150, 200, 250°F, and for 24 hours at 300°F. The original weight, the weight prior to oven-drying, and the dried weight for each specimen, is listed in Table 4.3.

A summary of the moisture absorbed weight percentages, for the 2-month, 6-month, and 12-month exposures, is given in Table 4.4. The overall average for all specimens, environments, and exposures, was   This corresponds to a minimum average porosity level in the Boral core of approximately   . The absorbed moisture decreased between 2-months and 6-months and increased between 6-months and one year. This may be the result of an initial decrease in porosity as corrosion products were generated in the core followed by a porosity increase as additional corrosion enlarged the pores. The greatest moisture absorption occurred in the open-edged specimens in the A environment. This specimen also showed the greatest number of pits and would, therefore, contain the greatest amount of material capable of absorbing moisture. The least moisture, on the average, was in the storage cell Boral plates, which may be due to their larger size and lower edge to volume ratio.

In Table 4.5, the corrosion weight gain percentages are summarized for all the specimens tested in the program. The values, in brackets, have been corrected to account for the fact that certain of the 6" x 4" Boral plates in the cell specimens contain a strip of solid aluminum along one edge. Since this strip did not contain the normal porous core structure, it could contribute weight gain only by external surface corrosion. To make valid comparisons, using these specimens, their weight was reduced by a factor corresponding to the reduced core volume. Under the assumption that the weight gain percentages are an indication of the extent of uniform corrosion in these specimens, the results presented in Table 4.5 show that the corrosion rates have decreased with increased exposure time. The results are plotted for each specimen type as a function of environment in Figures 4.4 through 4.6.

The weight gains are largest for the edge-sealed specimens in each environment. Similarly, they are the smallest for the storage cell specimens. In between, with very similar results, are the plain and open-edged specimens. The similar weight gains, experienced by these two (2) specimen types, show that the general corrosion is not accelerated due to coupling with stainless steel.

When the weight gain values for the storage cell specimens are considered on a semi-logarithmic scale, the relationship appears to be amenable to extrapolation, as shown in Figures 4.7 through 4.9. From these figures, the extrapolated weight gain percentage and the calculated percent of aluminum consumed after 40 years exposure, are:

4.4 Pitting

To evaluate the extent of pitting in the 12-month exposure specimens, the corrosion products were cleaned from the surfaces of a portion of one of the four (4) plates from each cell specimen. A summary of the pitting frequency and pit depth, for the 6-month and 12-month exposures, is given in Table 4.6. The pit diameter for the 12-month specimens is also given in the table.

Table 4.6 shows that the pitting characteristics after 12-months were very similar to those after 6-months. Those specimens and environment combinations which did not pit or showed little pitting tendency after 6-months, showed no or few pits after 12-months, however, those with significant pits after 6-months had a large number of pits after 12-months. Increased pitting was observed in the plain specimens in the A environment and in the edge-sealed specimens in the A and B environments. The other specimens showed nearly the same number of pits after 12-months as after 6-months.

The pit depth, however, increased with the extended 12-month exposure. In some cases where pits had not penetrated the aluminum clad in 6-months, they had done so after 12 months.

4.5 Metallography

Sections of Boral from each specimen were mounted and metallographically polished in order to observe the thickness of surface oxidation films, the depth of edge attack, the undercutting around drilled holes, and the nature of surface bulges. Sections were made along an edge for the plain and open-edged specimens, and through the drilled hole in the Boral for the edge-sealed and storage cell specimens. In addition, sections through bulges in the specimens were made to characterize these structures. The specimens were back-filled with epoxy under vacuum conditions to impregnate surface porosity, then rough polished on silicon carbide papers and final polished on diamond using automatic vibratory equipment.

4.5.1 Surface Corrosion Films

The surface corrosion films on several of the specimens were thick enough to measure using a filar eye piece at a magnification of The film thickness, as measured for these specimens, is listed in Table 4.7. The thickness for the C environment specimens was thickest, being a maximum of for the plain specimen. Where the bulge in this specimen caused the surface layer to break apart, the corrosion films were much thicker. Appendix B contains photographs showing the surface film in one area away from a bulge and, for comparison, on a bulge.

4.5.2 Edge Attack

Table 4.7 also shows the depth of corrosive attack at the Boral coupon edges in the plain and open-edged specimens. The attack was greatest in the A environment and was somewhat greater in the open-edged specimen than in the plain specimen. Only one specimen of the six (6) edge-sealed and storage cell types showed accelerated corrosion around the partially drilled leak simulating hole. This was the edge-sealed specimen in the C environment. The similarity in edge attack between the plain and open-edged specimens again indicates a lack of corrosion acceleration due to galvanic coupling of the Boral to stainless steel.

4.5.3 Bulges

Several bulges were observed on the 12-month exposure specimens. Similar bulges were not observed on specimens exposed for 2- or 6-months. Table 4.8 lists the number of bulges observed on each specimen. Photographs demonstrating bulged areas are shown on Figures 4.2 and 4.3.

The bulges are separations between the aluminum clad and the B_4C-aluminum matrix. They appear to result from gas pressure caused by internal corrosion. The corrosion of aluminum would generate hydrogen gas following the reaction

$$2Al + 3H_2O \longrightarrow Al_2O_3 + 3H_2.$$

Such gas generation has been observed in the edge-sealed and storage cell specimens. To generate a bulge would require sealing of the edges with corrosion products to enable the internal gas pressure to increase sufficiently to expand the ten mil aluminum cladding. The edge-sealed specimens each had four (4) bulges. These specimens also showed the largest corrosion weight gains which could result in the sealing of edges in these specimens.

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