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TECHNICAL DIVISION
SAVANNAH RIVER LABORATORY

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DPST-72-371

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MEMORANDUM

TO: R. T. HUNTOON

FROM: R. S. ONDREJCIN R.S.O.

[redacted]

CORROSION OF 8001 ALUMINUM FUEL CLADDING

INTRODUCTION

A program to evaluate the effects of flow, temperature, time, and heat flux on aqueous corrosion of aluminum alloys is in progress at CMX and involves both the Nuclear Materials and Reactor Engineering Divisions. Part of the program involves evaluation of the corrosion behavior of the 8001 aluminum fuel cladding presently used in SRP reactors. The corrosion tests are conducted in a corrosion loop which can be operated at heat fluxes above 10^6 pcu/(hr)(ft^2) over a range of water velocities and temperatures. This memorandum describes studies made on 8001 aluminum to determine the effect of the annealing treatment used for nonbond testing on corrosion behavior under simulated reactor conditions.

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SUMMARY

Corrosion testing of 8001 aluminum under simulated reactor conditions indicates that annealing Mark 18 fuel tubes for 15 minutes at 400°C for nonbond testing does not adversely affect in-reactor corrosion rates of the 8001 cladding. The corrosion rate of 8001 in the as-fabricated condition was slightly higher than in the annealed condition, even when annealing was far in excess of that used for nonbond testing. In addition, heat transfer and oxide growth calculations showed that no adverse effects would be expected from nonbond testing of Mark 14 fuel tubes. Other elements that operate under less severe conditions than Mark 18 could also be nonbond tested without damage.

The "black" oxide found on Mark 16 elements[1] was reproduced in the corrosion loop and was caused by higher than normal operating temperatures.

DISCUSSION

Evaluation of Aluminum Structure

"Dummy" Mark 18 outer fuel tubes of 8001 aluminum clad in 8001 were fabricated by the Raw Materials Department. Reactor Engineering Division personnel observed the fabrication and later heat treated sections of the tubes for up to 420 minutes at 400°C. Fifteen minutes at 400°C would be used for nonbond testing of a Mark 18 element; tubes that were heated for 420 minutes were evaluated in these tests, as an extreme case of annealing that might occur to cladding in reactor after a long time at high heat flux. Any effect on corrosion of the heat treatment during nonbond testing should also be magnified by such a long heat treatment.

The microstructure of 8001 was characterized by both light microscopy and electron microscopy. In the as-fabricated condition, grains were elongated in the direction of extrusion, Figure 1A. Heat treatment slightly above Mark 18 operation temperatures caused complete recrystallization over the entire cladding thickness (Figure 1B). Distinct changes in dislocation substructure accompany the recrystallization; the dense dislocation tangles and subcell boundaries characteristic of the as-fabricated cladding (Figure 1C) disappeared during recrystallization leaving grain or subgrain boundaries with few observable dislocations (Figure 1D). Theoretically, the as-fabricated cladding should corrode faster than the annealed cladding because of the stored energy in the metal in the form of dislocation tangles and other lattice defects.

Corrosion Loop Evaluation

Sections of the dummy Mark 18 fuel tubes of 8001 cores clad with 8001 were tested in the as-fabricated and heat treated (420 minutes at 400°C) conditions. Corrosion test conditions (Table I) were chosen to simulate the Mark 18 exposure except that the test time was longer and the pH was slightly higher than encountered in-reactor (6.5 vs 5.2).

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TABLE I

LOOP OPERATING CONDITIONS

Heat Flux (pcu/(hr)(ft^2))	$1.0 \pm 0.06 \times 10^6$
Water Velocity (ft/sec)	50 ±3
Dissolved O_2 (ppm)	6-10
Cooling Water Temperature (°C)	50 ±3
Conductivity (μmho/cm)	<0.5
pH	6.2-6.9
Run Time (days)	14

The oxide films that formed on the heat treated and the as-fabricated specimens during the loop tests had several different characteristics (see following section). The heat treated metal grew a relatively thin (13 ±1 μm) oxide while the as-fabricated metal grew a somewhat thicker (17 ±1 μm) oxide.

These results indicate that nonbond testing by annealing at 400°C for 15 minutes would not adversely affect corrosion rates of the cladding of Mark 18 fuel. Other fuel elements that do not operate under as severe conditions as the Mark 18 could also be nonbond tested by this heat treatment. The appendix gives calculations comparing Mark 18 and Mark 14 operating conditions. Although the Mark 14 runs much longer than the Mark 18, the temperatures at oxide-water and metal-oxide interfaces are lower. Rapid corrosion is strongly temperature dependent; nonbond testing of Mark 14 fuel elements should not adversely affect their corrosion rate.

Oxide Film Characteristics

The corrosion resistance of 8001 is attributed to fine, uniform dispersions of second phase iron and nickel aluminides that are cathodic to the matrix. The function of the second phase is to allow hydrogen ion reduction before the ions reach the metal-oxide interface and thereby prevent the hydrogen gas from disrupting the protective oxide by bubble formation at the metal-oxide interface. Figure 2 shows a few of the larger cathodic particles that are retained in the oxide film of 8001. The film was grown in the loop under conditions similar to those shown in Table I except that the exposure time was 6.8 days. The cathodic particles are apparently oxidized as the specimen continues to corrode.

The oxides formed under the conditions shown in Table I showed distinct differences for the as-fabricated and heat treated specimens. The oxide on the as-fabricated specimens was highly stressed and fragmented, particularly at the outer surface, Figure 3a. The oxide on the heat treated metal was thinner and fragments were blocky in appearance, about as thick as the oxide itself, Figure 3b. In both

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cases, the fractures extended through the oxide to the metal surface. These differences may be attributable to differences in residual stresses on the specimen, as it is well known that such stresses are transferred to oxide films as the metal oxidizes. The effect of these differences on turbidity in the moderator is unknown.

Examination of the oxide films by X-ray techniques showed that the oxides were primarily amorphous, with 10% of the oxide crystallized. The crystalline portion was a high temperature form of alumina, boehmite ($\alpha Al_2O_3 \cdot H_2O$); this structure is normally formed at >80°C. Although the bulk cooling water temperature was only 50°C the calculated oxide-water interface temperature was 130-160°C. The calculated oxide-metal interface temperature was 55°C above the oxide-water interface temperature, or 185-215°C, thus accounting for the high temperature oxide. A comparison of the X-ray diffraction peak heights of weighed amounts of boehmite and the peak heights of the sample indicated the boehmite was only 1.5 μm thick. Because the oxide film thicknesses were measured at 12-18 μm (Figure 3), apparently only about 10% of the oxide was crystalline.

If the cooling water temperature was raised to 75°C instead of 50°C, while the loop was operated at a heat flux of 10^6 pcu/(hr)(ft^2) the oxide gradually darkened and was black at the end of three days. Such operating conditions are more severe than normal reactor conditions for the Mark 18, which are: a coolant temperature of <75°C at the position of maximum heat flux ~10^6 pcu/(hr)(ft^2) or a coolant temperature of 80°C maximum at a lower heat flux.

"Black" oxide has been reported[1] for some areas of cladding on Mark 16 fuel in the C-1 cycle. The assumption that the black oxide formed because of "dogboning" of the fuel is supported by its formation in the loop under severe conditions, thus indicating that the black areas operated at a higher temperature and higher heat flux than the rest of the fuel. A cross section of the thick 36 μm (1.4 mil) "black" oxide formed in 75°C cooling water is shown in Figure 4. This oxide, physically stripped from its base metal and examined by X-ray diffraction technique, was found to be nearly identical to the normal oxide (boehmite) formed under less severe conditions. The estimated water-oxide interface temperature was 185°C. The calculated metal-oxide interface temperature was 300°C and no intergranular attack of the 8001 was observed.

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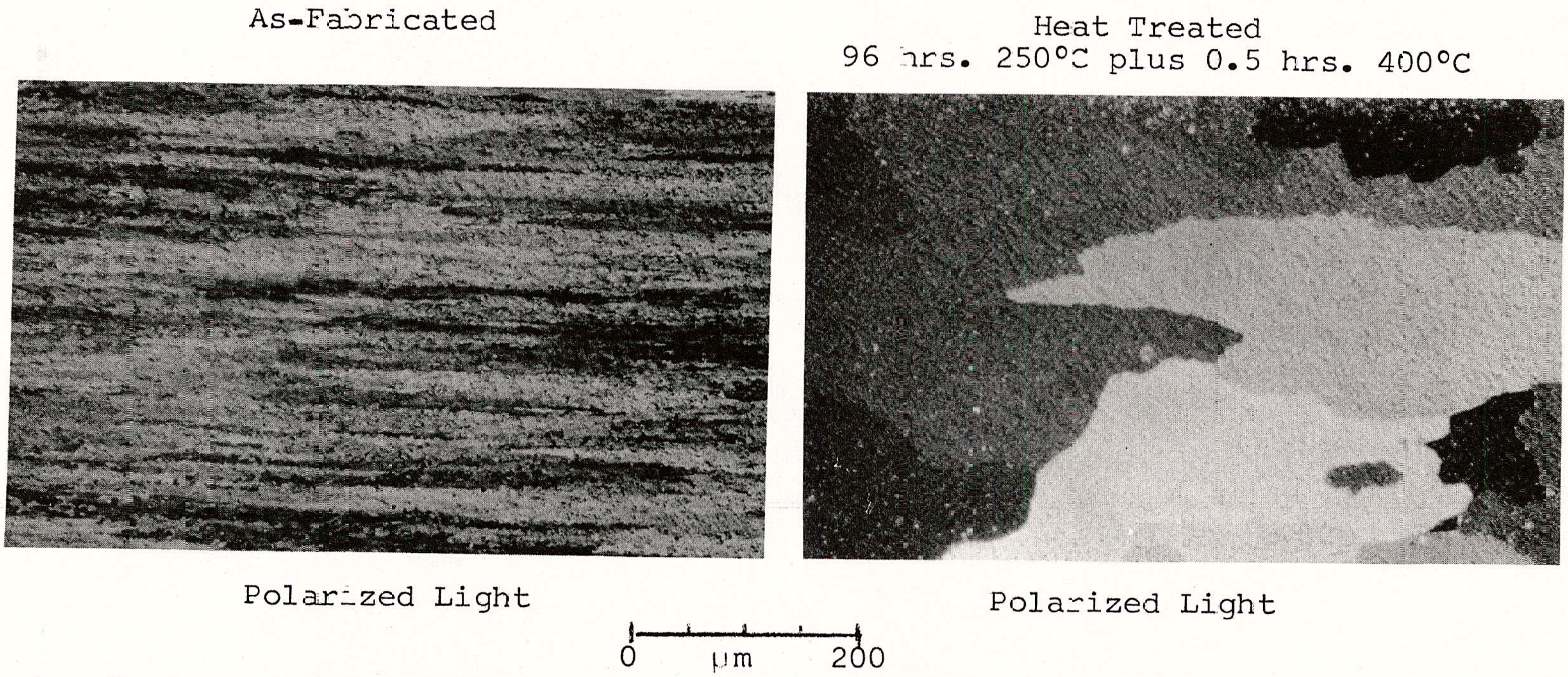
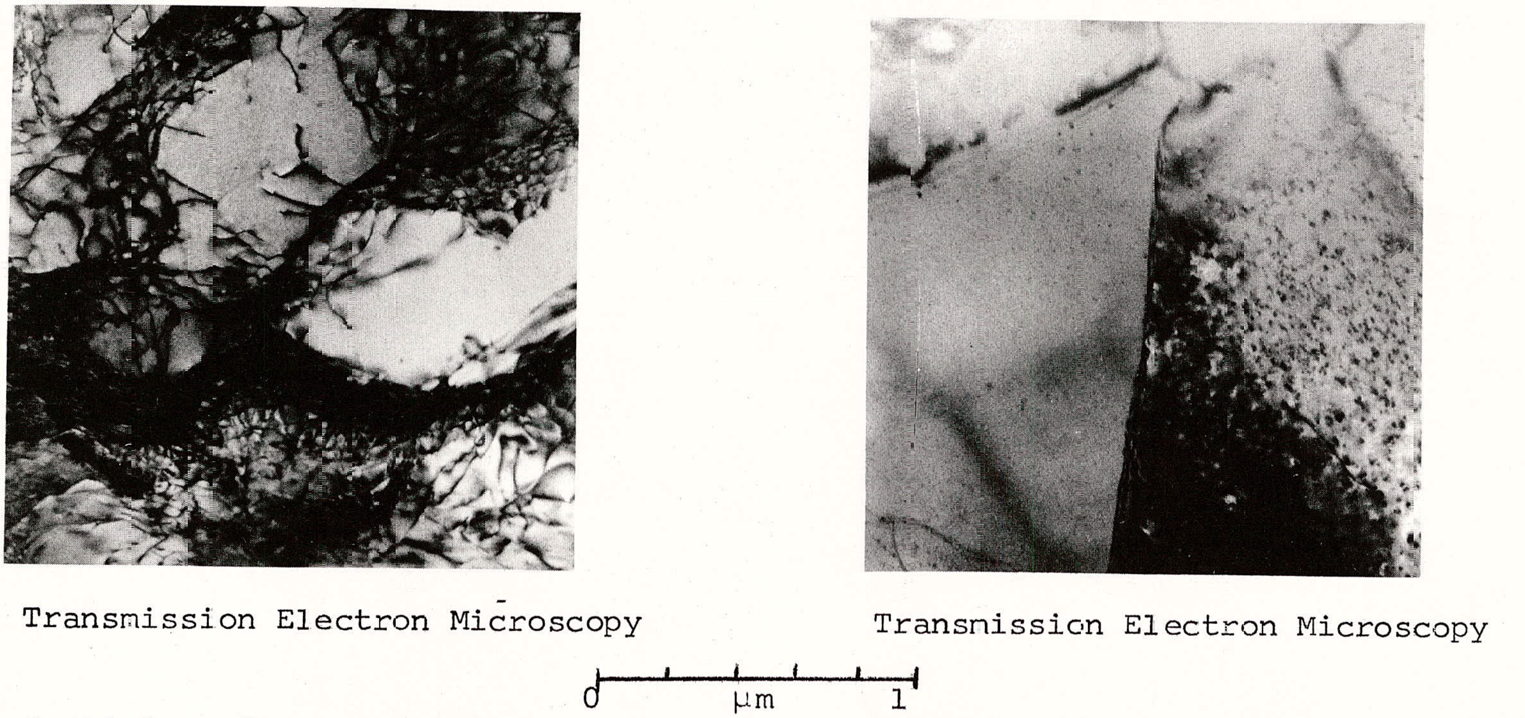


A. Grains elongated during coextrusion

B. Grains fully recrystallized into equiaxed structure



C. Dislocation tangles and subcells

D. Clean boundaries few dislocations

FIG 1. STRUCTURES OF HEAT TREATED 8001 ALUMINUM

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[redacted]

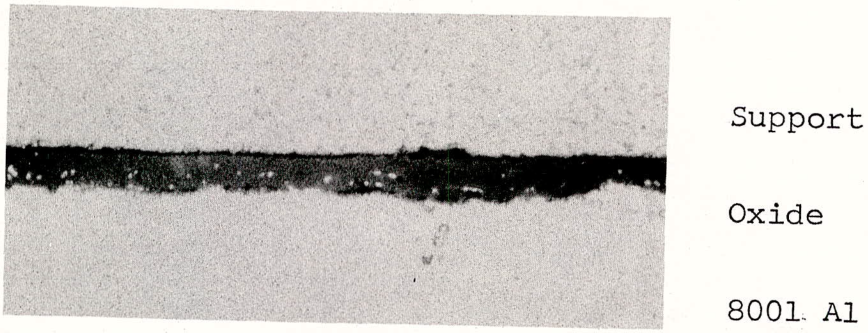
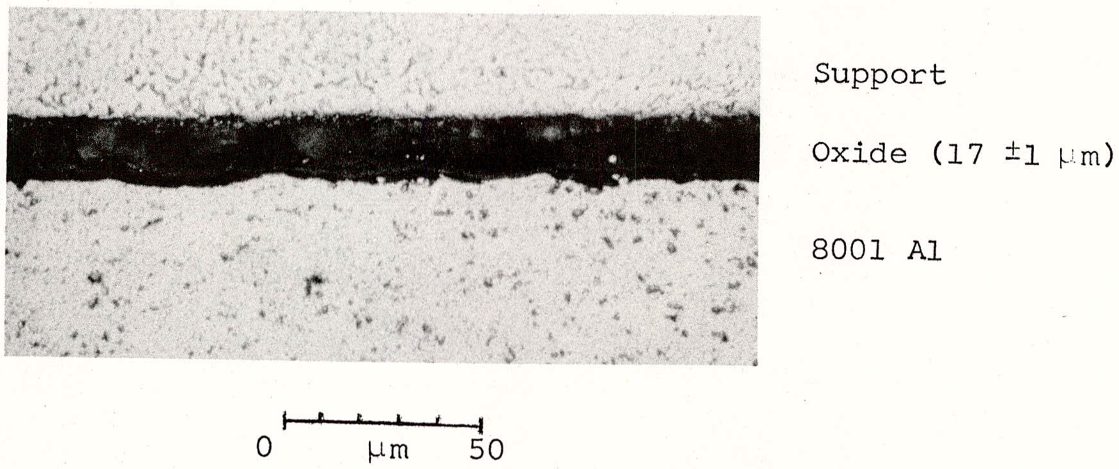
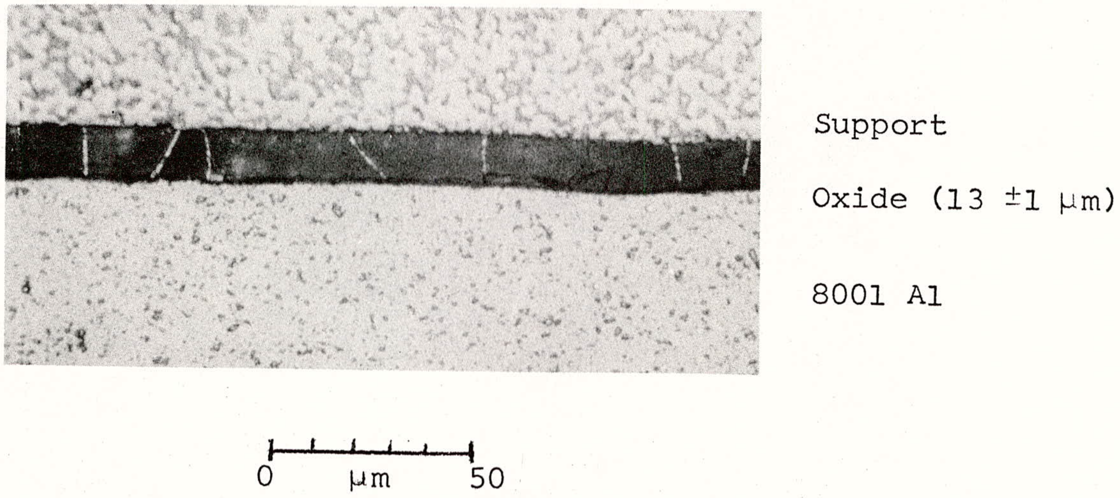


FIG 2. CATHODIC ALUMINIDES IN OXIDE FILM
(Note nickel and iron aluminides near metal surface have not been oxidized.)

[redacted]



a. As-Fabricated



b. Heat Treated
420 min at 400°C

FIG 3. STRUCTURE OF OXIDES ON 8001 ALUMINUM

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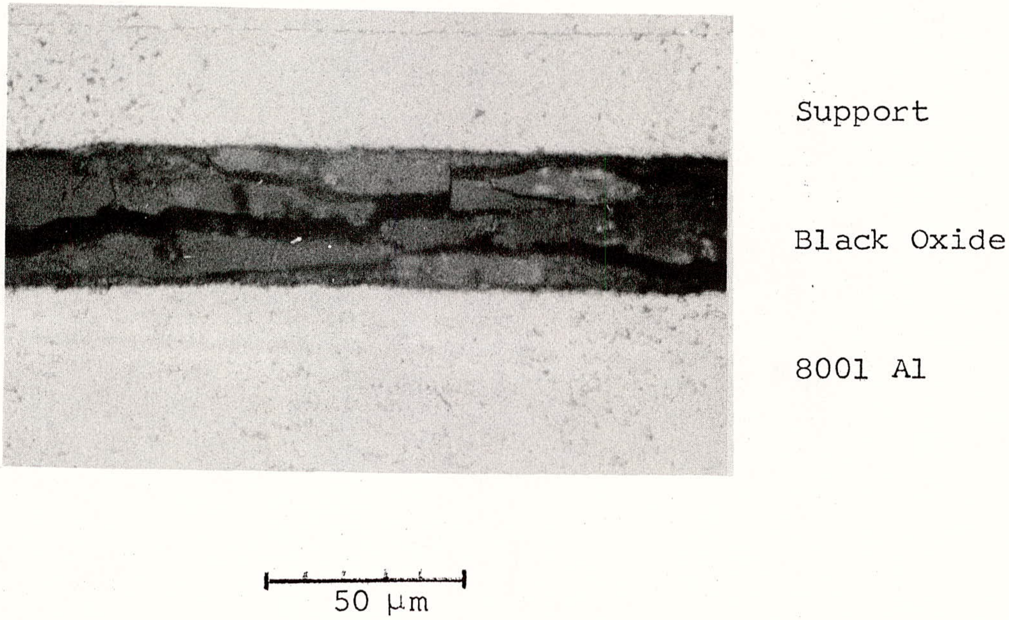

FIG 4. "BLACK" ALUMINUM OXIDE (A high temperature rapid oxidation product)

[redacted]

[redacted]

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2. J. C. Griess, H. C. Savage and J. L. English, "Effect of Heat Flux on Corrosion of Aluminum By Water, Part IV. Tests Relative to the Advanced Test Reactor and Correlation with Previous Results" ORNL-3541 February 1964.

3. DPSP 65-1-11, Works Technical Department November 1965 (Secret)

[redacted]

APPENDIX

OXIDE INTERFACE TEMPERATURES AND THICKNESS

	Water-Oxide Interface Temp. (°C)		Metal-Oxide Interface Temp. (°C)		Oxide Thickness µm (mils)	
	Ave.	Max.	Ave.	Max.	Ave.	Max.
Mark 18(a)	130	180	145	230	4.3(0.2)	15(0.6)
Mark 14(b)	105	150	140	170	32(1.3)	55(2.2)

(a) Assumes 1×10^6 pcu/(hr)(ft^2) for 4 days, cooling water 30-80°C, with 50°C average.

(b) Assumes 0.33×10^6 pcu/(hr)(ft^2) for 90 days, cooling water 40-110°C with 75°C average.

All water-oxide interface temperatures were calculated on the basis of the Colburn equation:

$$\frac{h}{c_p G}\left(\frac{\mu c_p}{k}\right)^{2/3} = \frac{0.023}{(G\ D/\mu)^{0.2}}$$

where,

h = oxide heat transfer coeff., pcu/(hr)(ft^2)(°C)

c_p = water heat capacity, pcu/(lb)(°C)

G = water mass flow rate, lbs/(ft^2)(hr)

μ = water viscosity, lbs/(ft)(hr)

k = water thermal conductivity, pcu/(hr)(ft)(°C)

D = twice channel gap thickness, ft.

in conjunction with Newton's Law of Cooling

$$Q/A = h(t_c - t_f)$$

where,

Q/A = heat flux, pcu/(hr)(ft^2)

h = oxide heat transfer coefficient, pcu/(hr)(ft^2)(°C)

t_c = water-oxide interface temperature, °C

t_f = bulk cooling water temperature, °C

[redacted]

Metal-oxide interface temperatures were calculated by the Fourier Heat Conduction equation

$$Q/A = K_c \frac{t_s - t_c}{C}$$

where,

Q/A = heat flux, pcu/(hr)(ft^2)

K_c = oxide thermal conductivity, 1.0 pcu/(hr)(ft)(°C)

t_s = metal-oxide interface temperature, °C

t_c = water-oxide interface temperature, °C

C = oxide thickness, ft

Mark 18 oxide thicknesses were calculated by the Griess correlation$^{(2)}$

$$X = 433(\theta)^{0.778}\exp(-4600/K)$$

where,

X = oxide thickness, mils

θ = time of oxide growth, hours

K = absolute temperature of water-oxide interface, °K

Mark 14 oxide thicknesses were calculated by the Kritz correlation$^{(3)}$

$$C = 17.3\ (\theta)^{0.778}\exp(-1880/K)$$

where,

C = oxide thickness, mils

Q/A = heat flux, 10^6 pcu/(hr)(ft^2)

θ = time of oxide growth, days

K = absolute temperature of water-oxide interface, °K

[redacted]