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HEAT TRANSFER EFFECTS ON THE CORROSION OF ZIRCONIUM AND SOME ALLOYS

Louis A. Waldman
Paul Cohen

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ABSTRACT

A study has been made of the quantitative relationship between heat transfer and the corrosion of zirconium alloys through an investigation of accelerated corrosion rates as a function of thermal gradients in an oxide film. This treatment was based on available isothermal corrosion data and on heat transfer data obtained by direct measurements on the corroded metal.

An application of this analysis to the PWR reference design~~s~~ indicates that heat-transfer corrosion does not pose a problem for the core lifetimes under consideration. However, the analysis indicates that future reactors designed for higher fluxes and surface temperatures may be limited in their operation, especially for the case of heavy fouling on the corroded metal.

Heat Transfer Effects on the Corrosion of Zirconium and Some Alloys

I. Introduction

In applications at high heat transfer rates, consideration must be given to possible acceleration of the corrosion process because of thermal gradients in the oxide film on the metal, and care must be exercised in applying isothermal corrosion data to such cases. This is particularly true with regard to zirconium and some of its alloys as applied to heat transfer surfaces in water-cooled reactors.

A direct measurement of this effect on pure zirconium was attempted at the Westinghouse Atomic Power Division, Bettis Site early in the development program with the following results:

(1) Only two-hundred and fifty hours of testing at 1,150,000 Btu per hr and ft^2 could be obtained because of local electrolytic corrosion on the specimens due to the 60 cycle alternating current used for heating.

(2) In this test period, the temperature drop observed in the oxide film was consistent with the known corrosion behavior of zirconium and estimates of the conductivity of the oxide.

(3) For the proposed application conditions, zirconium was not susceptible to accelerated corrosion due to heat transfer.

When it was decided to manufacture subsequent cores from zirconium alloys, consideration was given to this problem as soon as pertinent corrosion data for the alloys under consideration became available. It was fairly certain from the isothermal corrosion data, and estimates of oxide conductivity that zircaloy 1[1] was not suitable for application whereas Zircaloy 2 was acceptable. A program was started to confirm these opinions, and to establish more definitely the conditions of applicability of these materials. Because of the uncertainty of finding a solution to the electrolytic corrosion problem, the direct experimental approach was temporarily discarded in favor of the synthetic approach of combining the results of isothermal corrosion data with experimentally determined heat transfer properties of the corrosion film. Since an extensive corrosion test program for the zirconium alloys was planned at the Atomic Power Division, it was only necessary to obtain the heat transfer properties of the scale*. A subcontract for this purpose (14-302) was awarded to the Research and Development Laboratories of the Babcock and Wilcox Company, Alliance, Ohio. The Babcock and Wilcox tests are separately reported[2], and the pertinent test results are analyzed in the Appendix. The combined data from these sources are utilized in this report to determine the corrosion behavior of zirconium alloys under heat transfer conditions.

II. Corrosion Theory and Data for Zirconium Alloys

The mechanism of corrosion of zirconium and its alloys has been studied in detail[3][4], and is briefly summarized as follows. Corrosion proceeds first by a thin-film mechanism in which the controlling step is believed to be the solid state diffusion of ionic oxygen through the non-porous film. As the film thickness increases, the rate of growth decreases, correspondingly. At a film thickness characteristic of the temperature and material, the corrosion rate suddenly "breaks away" to a high and constant rate. The constant breakaway corrosion

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* Scale is defined herein as the corrosion film on the metal. The term "fouling", used in later sections of the report, refers to extraneous deposition.

rates at isothermal conditions have been explained by postulating that the breakaway scale consists of a porous layer, attached to a thin, non-porous layer of constant thickness adjacent to the metal oxide interface. Essentially constant diffusion of ionic oxygen through the non-porous layer determines the constant corrosion rate. Before breakaway, the films are so thin as to be essentially isothermal. After breakaway, the corrosion rate should be determined by the temperature at or near the metal oxide interface. The pertinent data are shown in Tables 1 and 2.

TABLE 1

Equations for the Thin Film Corrosion [4] of Zircaloy 2

Temperature, °F	Equation	Time to Breakaway
(1) 550 saturated	$\log w = 0.24 \log \Theta + 0.64$	
(2) 600 saturated	$\log w = 0.27 \log \Theta + 0.74$	
(3) 680 saturated	$\log w = 0.38 \log \Theta + 0.73$	110 days
(4) 750 (steam, 1500psi)	$\log w = 0.40 \log \Theta + 1.02$	30 days

Θ = time, days

w = weight gain, mg/dm^2

TABLE 2

Breakaway Corrosion Rates of Zircaloy 2 [5]

Temperature, °F	Corrosion Rate after breakaway, mg/dm^2 day	Weight Gain at Breakaway mg/dm^2
600 saturated	0.16	- - - -
680 saturated	0.40	33
750, steam, 1500 psi	1.0	39

The breakaway corrosion data are plotted as a function of absolute temperature in Figure 1. The equation representing the plot is

$$\frac{dw}{d\theta} = Ae^{-B/T} \qquad (5)$$

where w = weight gain, mg/dm^2

A, B are constants (see Figure 1)

T = absolute temperature, ° Rankine

θ = time, days

Equation (5) conforms with the Arrhenuis equation for the variation of reaction rate constants with temperature.

III. Heat Transfer Relationships during Corrosion

The metal/oxide interface temperature, a function of scale thickness, heat flux and surface temperature, may be represented exactly for a flat plate and, with little error, for other geometries, at the scale thicknesses under consideration, as,

$$(6) \qquad t_i = t_s + \frac{q\delta}{k}$$

where t_i = interface temperature, °F

t_s = surface temperature, °F

q = heat flux, Btu/hr x ft^2

δ = scale thickness, ft.

k = thermal conductivity of scale, Btu/hr x ft^2 x °F/ft

= 0.79 Btu/hr x ft^2 x °F/ft (See Appendix)

or

$$(7) \qquad T_i = T_s + \frac{q\delta}{k}$$

where T_i = interfacial temperature, °R

T_s = surface temperature, °R

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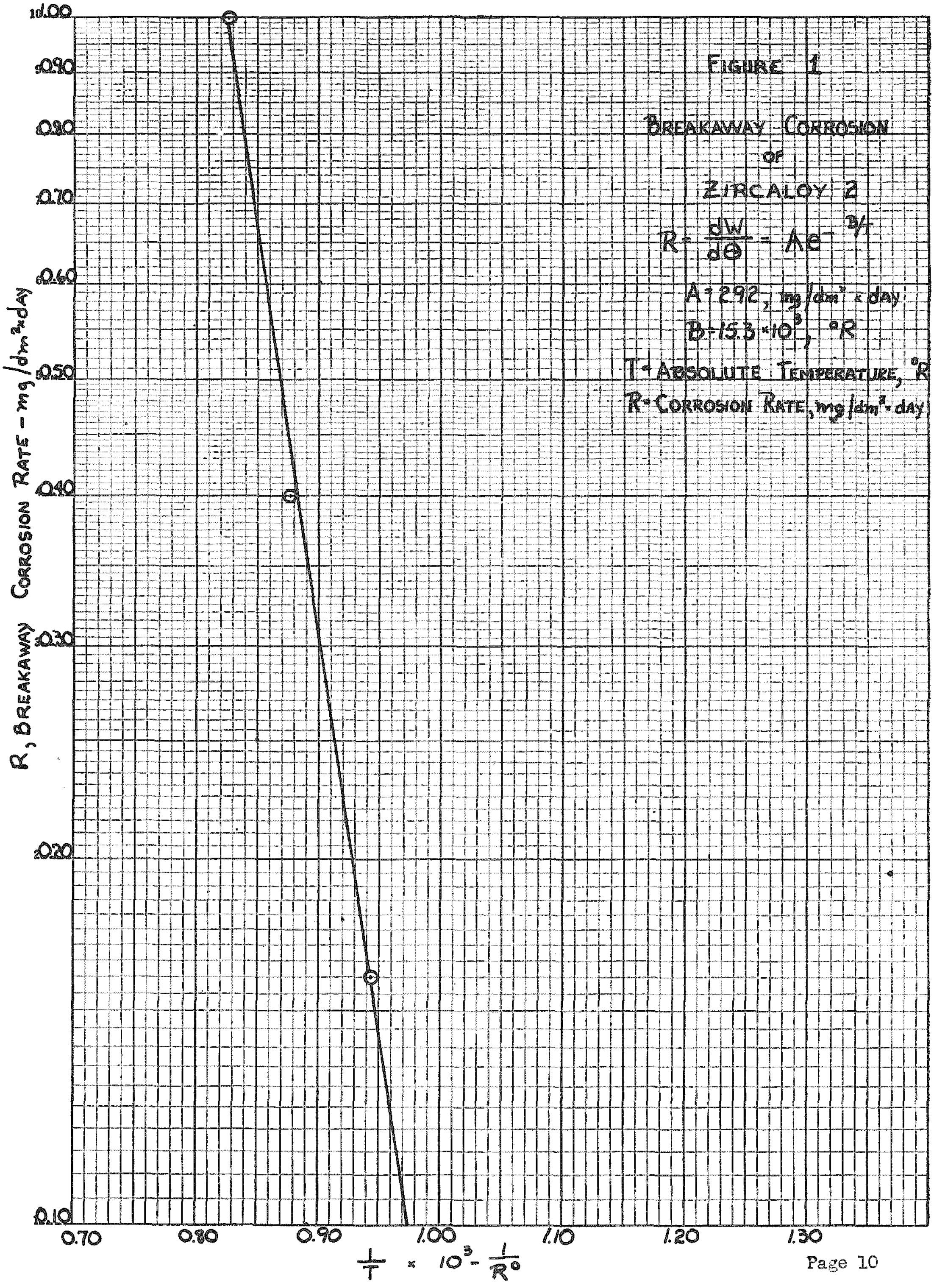

FIGURE 1

BREAKAWAY CORROSION
OF
ZIRCALOY 2

$$R = \frac{dW}{d\Theta} = Ae^{-B/T}$$

$A = 292$, mg/dm² × day

$B = 15.3 \times 10^3$, °R

T = ABSOLUTE TEMPERATURE, °R

R = CORROSION RATE, mg/dm² × day

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Substituting (7) in (5):

$$(8) \qquad \frac{dw}{d\theta} = Ae^{-B/(T_s + q\delta/k)}$$

The relationship between scale thickness and weight gain is given by the following:

$$(9) \quad w = \delta\rho \times (2.54)(12)\ \text{cm/ft} \times \frac{100\ \text{cm}^2}{\text{dm}^2} \times \frac{(O_2)}{(ZrO_2)} \times \frac{1000\ \text{mg}}{\text{gm}}$$

or $\delta = 0.225 \times 10^{-6}\ w$

where ρ = density of scale = 5.6 gm/cm^3 [9]

$\frac{(O_2)}{(ZrO_2)}$ = $\frac{\text{Molecular weight of oxygen}}{\text{Molecular weight of } ZrO_2}$

w = weight gain in mg/dm^2

Substituting (9) in equation (8) and letting

$m = 0.225 \times 10^{-6}\ A$

$u = q/k$

then:

$$(10) \qquad \frac{d\delta}{d\theta} = me^{-(B/T_s + u\delta)}$$

where m, B and u are constants defined above.

Since the corrosion data are given as either time to breakaway or weight gain at breakaway , then by letting $\theta_b = \theta - \theta_t$ where θ_t is the time to start of breakaway, θ_b, the time after breakaway corrosion beings, and θ, the total corrosion time; and letting δ_t equal the scale thickness before breakaway the relationship between scale thickness and time becomes

$$(11) \qquad \frac{1}{m}\int_{\delta_t}^{\delta_b} e^{(B/T_s + u\delta)}\, d\delta = \int_0^{\theta_b} d\theta$$

Equation (11) was evaluated by graphical integration, since the analytical solution resulted in a series that converged too slowly to be useful for calculation purposes.

IV. Results

A. Corrosion Without Extraneous Deposits

Figure 2 is a plot of heat throughput corrosion effects on Zircaloy-2 determined by means of equation (11). The corresponding interfacial temperatures (metal/oxide) are plotted in Figure 3. Since the temperature drop across the scale significantly influences the corrosion rate for breakaway conditions only, no problem exists with respect to heat-throughput corrosion of Zircaloy-2 (550.F maximum surface temperature with a corresponding heat flux of 500,000 Btu/hr x ft²). An exposure well beyond the expected core lifetime would be required at 550°F before breakaway corrosion begins.* Likewise, for PWR, breakaway would not occur before reactor lifetime at full power is reached. Curve A of Figure 2 shows the accelerated corrosion rates at longer exposure times.

Relationships such as those shown in Figure 2 must be evaluated in terms of (1) corrosion rates such that the clad material is significantly weakened, (2) excessive temperatures in the fuel material due to the temperature drop across the scale. In order to avoid a phase transformation in U-Mo as a result of thermal cycling, it would be advisable to maintain the maximum fuel temperature below 1100°F. For a 0.304" O.D. rod with a 30 mil clad, PWR operating parameters indicate that the maximum fuel temperature may be above 1100°F for a small percentage of the rods.** Considerations of the temperature drop across the scale would increase the number of fuel elements falling in this category. Also, higher temperatures at the clad-core interface must be carefully considered as soon as

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* E.G., for $w = 33$ mg/dm², $\Theta \cong 780$ days from equation (2) corresponding to 600°F exposure. It should be noted, however, that no experimental data has been determined as yet for breakaway corrosion of Zircaloy-2 at temperatures below 680°F.

** The actual number is not presently known since the only available thermal conductivity values for U-Mo were measured at low temperatures (< 100°C).

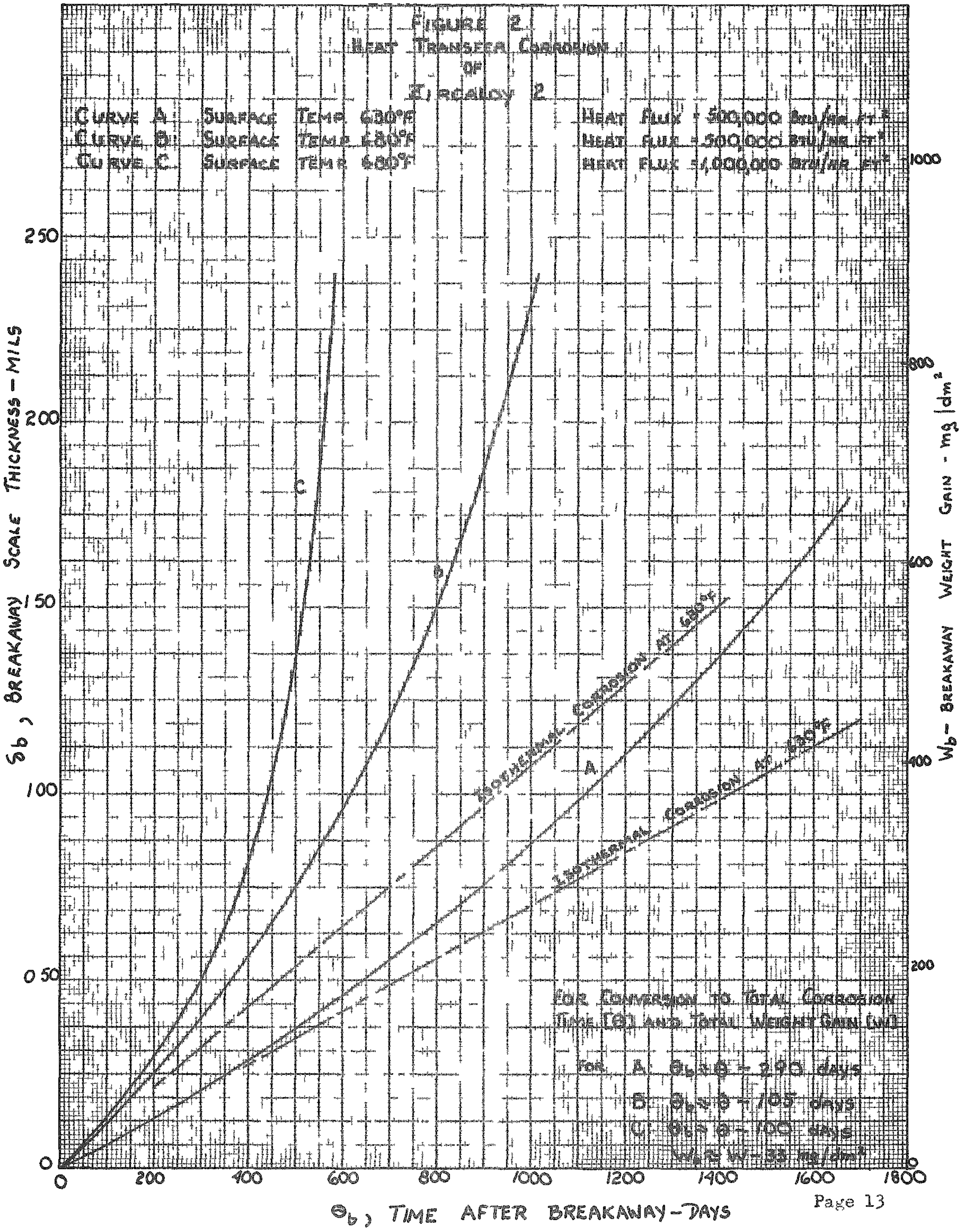

FIGURE 2
HEAT TRANSFER CORROSION
OF
ZIRCALOY 2

FOR CONVERSION TO TOTAL CORROSION TIME [Θ] AND TOTAL WEIGHT GAIN [W]

FOR A $\Theta_b = \Theta - 290$ days
B $\Theta_b = \Theta - 105$ days
C $\Theta_b = \Theta - 100$ days
$W_b = W - 33$ mg/dm²

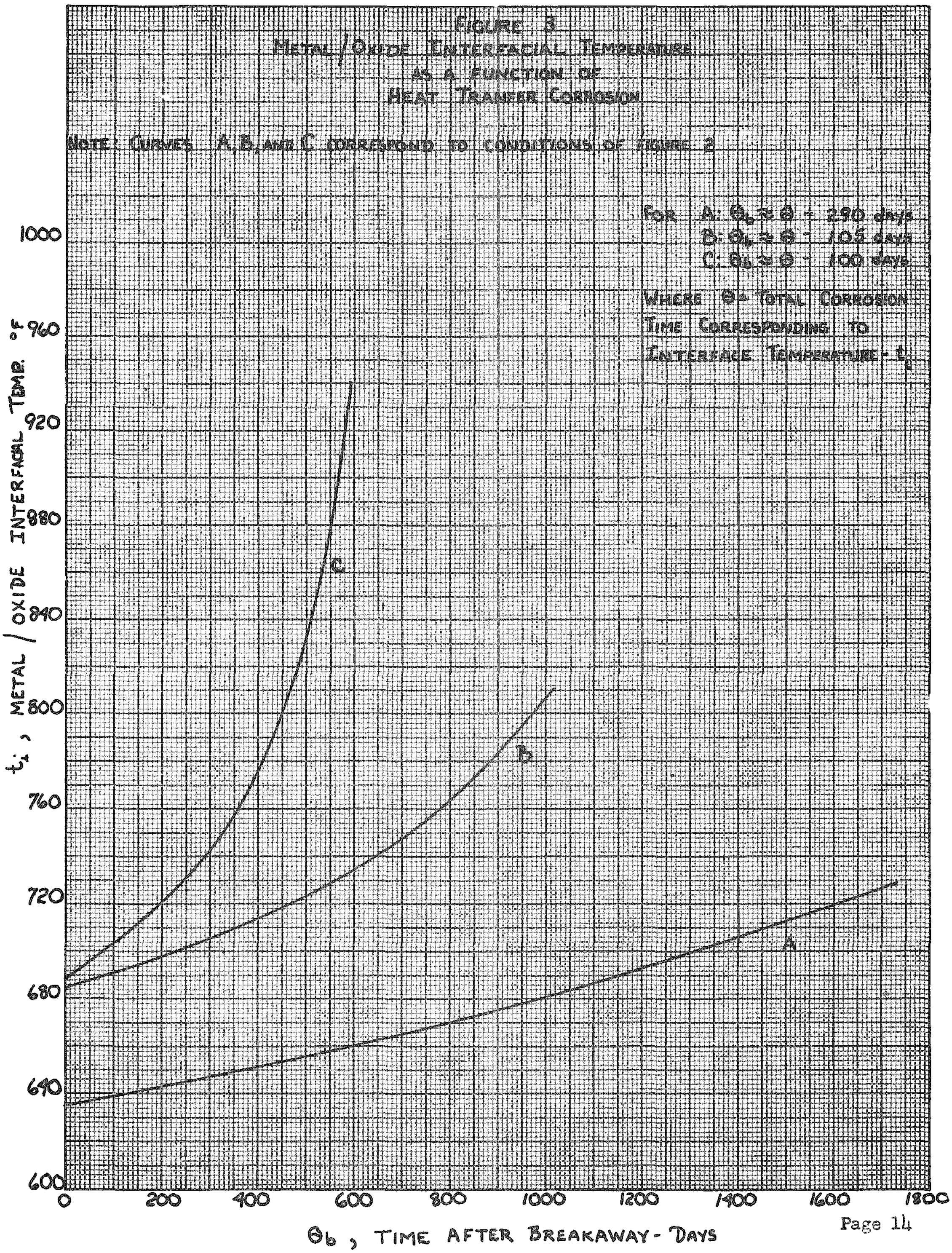

FIGURE 3
METAL/OXIDE INTERFACIAL TEMPERATURE
AS A FUNCTION OF
HEAT TRANFER CORROSION

NOTE: CURVES A, B, AND C CORRESPOND TO CONDITIONS OF FIGURE 2

FOR A: $\Theta_b \approx \Theta - 290$ days
B: $\Theta_b \approx \Theta - 105$ days
C: $\Theta_b \approx \Theta - 100$ days

WHERE Θ = TOTAL CORROSION TIME CORRESPONDING TO INTERFACE TEMPERATURE - t_i

pertinent data on the corrosion resistance of U-Mo alloys are established. Numerical values for these higher temperatures can be determined from Figure 3. The temperature drop across the scale is determined simply by subtracting the temperature at $\Theta_b = 0$ from the corresponding temperature at a given Θ_b. This temperature drop would be added to the temperature distribution within the fuel element determined for the case of no corrosion.

The total amount of Zircaloy clad corroded after a period corresponding to the maximum corrosion time shown in Curve A of Figure 1 would be about 1 mil and the temperature drop across the scale about 95°F. Hence, neither (1) nor (2) are indicated for the PWR at times well beyond the anticipated core lifetime.

At this point, it is interesting to note heat-transfer corrosion effects on Zircaloy-1 as shown in Figure 4.* Assuming that breakaway corrosion begins shortly after reactor start-up (e.g., for the worst case reported, only seven days of thin film corrosion time for Zircaloy-1 at 650°F(6)), then it is apparent upon examining Figure 4 that it would be hazardous to contemplate operation at PWR conditions for periods greater than some 50 days (1200 hours). Figure 4 shows a weight gain of 1.78 gms/dm^2 at the end of 56.5 days of operation, corresponding to a temperature drop across the scale of 250°F and a reduction of 3 mils in clad thickness. Hence, excessive fuel temperatures may be encountered and the clad thickness significantly reduced after a short corrosion time. It is interesting to note in comparison that isothermal corrosion of Zircaloy-1 at the maximum PWR surface temperature would permit operation for a considerably longer time.

The utilization of Zircaloy-2 at higher temperatures and for longer lifetimes is subject to the restrictions shown in Curves B and C of Figure 2. At a surface temperature of 50°F above the maximum specified PWR surface temperature

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* The thermal conductivity found for the Zircaloy-2 scale was assumed for the Zircaloy-1 scale. Corrosion rates were determined from a plot similar to Figure 1 (e.g., 10 mg/dm^2 x day at 750°F).

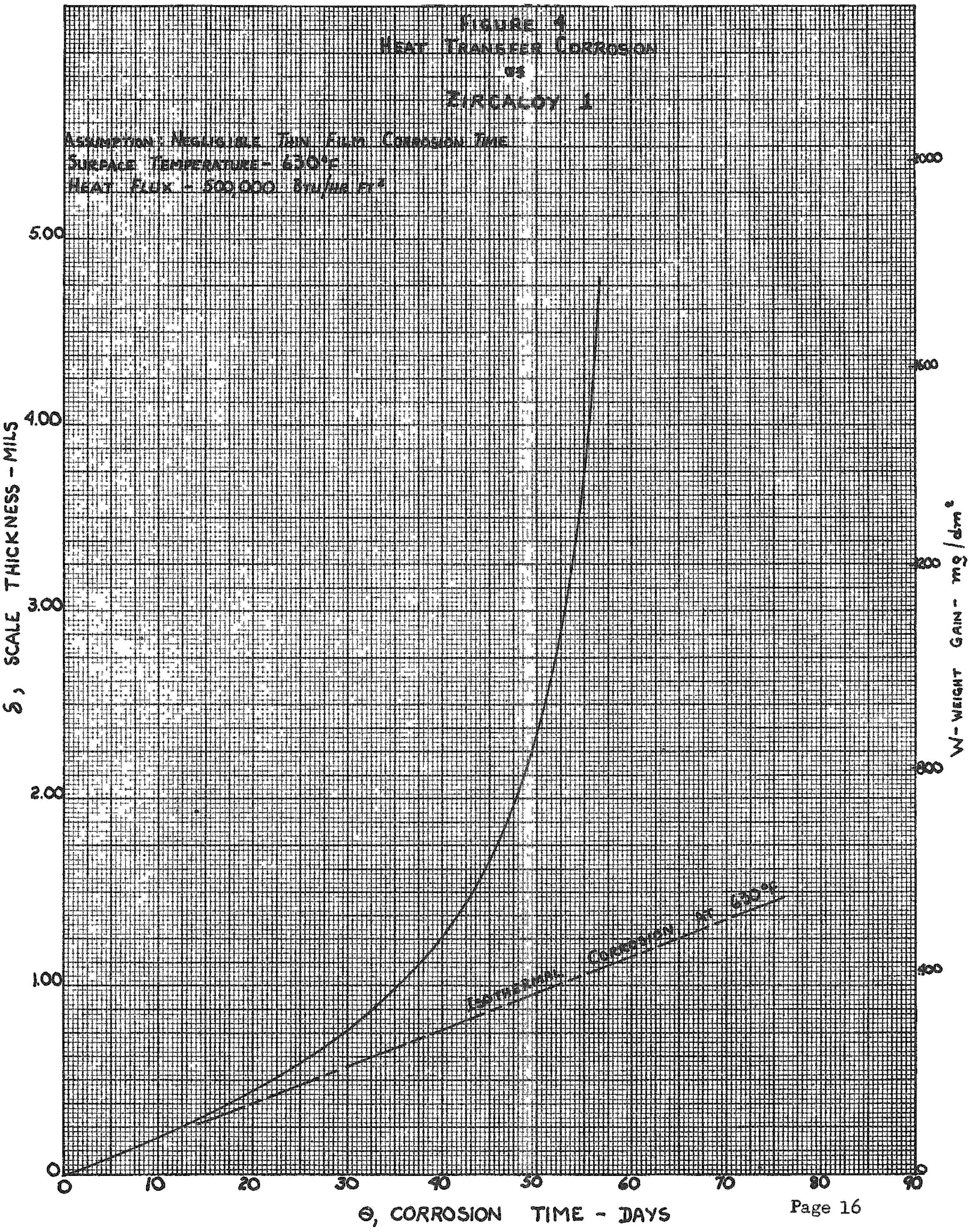

FIGURE 4
HEAT TRANSFER CORROSION
vs
ZIRCALOY 1

ASSUMPTION: NEGLIGIBLE THIN FILM CORROSION TIME
SURFACE TEMPERATURE - 630°F
HEAT FLUX - 500,000 BTU/HR FT²

and at PWR heat flux, a reduction of one mil in clad thickness and a 95°F temperature drop across the scale would occur after 950 days. If the heat flux corresponding to the maximum surface temperature of 680°F is doubled, the same corrosion level would be reached after some 500 days of operation and the temperature drop across the scale increased to 190°F. The rapid increase in the corrosion level with time shown by Zircaloy-1 in Figure 4 is characteristic of Curve C of Figure 3 as well. Accordingly, operation at this temperature and heat flux may be prohibitive for lifetimes greater than some 15,000 hours.

B. Fouling Considerations

The previous treatment does not include the effects of fouling. Since heat transfer parameters for characteristic deposits have not yet been determined, curves were calculated in Figure 5 for assumed fouling factors. It should be noted that fouling coefficients less than 5,000 to 10,000 Btu/hr x ft^2 x °F are extremely pessimistic. Accordingly, Figure 5 indicates that heavy fouling does not result in prohibitive corrosion levels for core lifetimes presently under consideration. In the cases considered in Figure 5, the interface temperatures between the deposit and heat transfer surface are above the reactor saturation temperatures for PWR. Formation of deposits under these conditions has not been explored and such effects as might be produced by boiling at the interface have not been taken into consideration. If it is assumed that the deposit is firmly attached to the surface even though the interface temperature is above saturation and all deposition occurs immediately after reactor start-up, then curves one through four in Figure 5 would conform to the conditions shown on the corresponding key.

The maximum fuel temperature should be limited to some 1100.F (as for the case of U-Mo) in order to avoid a U-Zr phase transformation.* Hence,

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* Thermal stress considerations may be another limitation for fuel plate geometry.

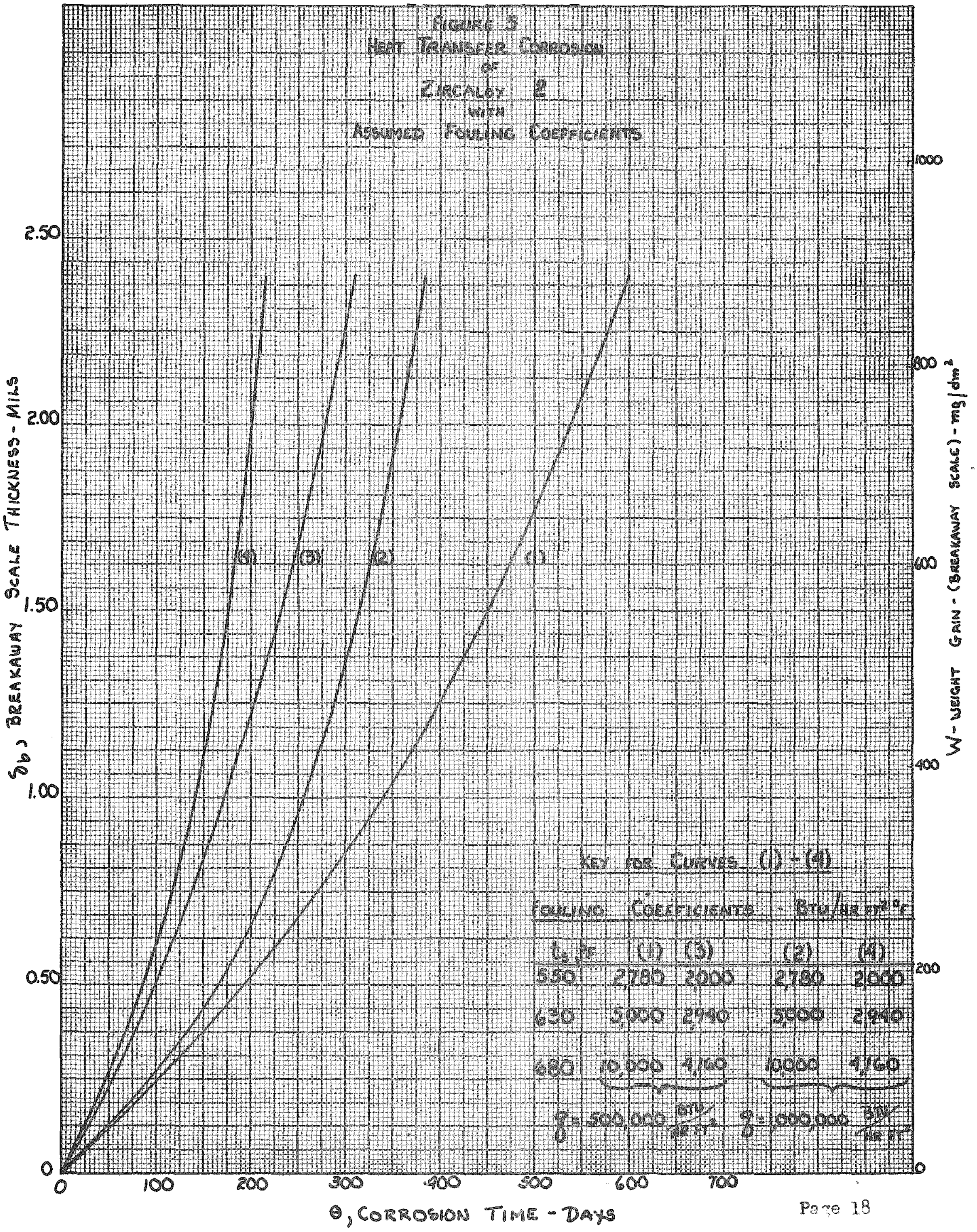

FIGURE 5
HEAT TRANSFER CORROSION
OF
ZIRCALOY 2
WITH
ASSUMED FOULING COEFFICIENTS

KEY FOR CURVES (1) - (4)

FOULING COEFFICIENTS - BTU/HR FT² °F

t_s, °F	(1)	(3)	(2)	(4)
550	2,780	2,000	2,780	2,000
630	5,000	2,940	5,000	2,940
680	10,000	4,160	10,000	4,160

$\underbrace{(1)\ (3)}_{q = 500{,}000\ \frac{BTU}{HR\ FT^2}}$ $\underbrace{(2)\ (4)}_{q = 1{,}000{,}000\ \frac{BTU}{HR\ FT^2}}$

for a fouling coefficient of 2000 Btu/hr x ft^2 x ^{o}F, a reactor could operate for some 270 days, corresponding to a corrosion weight gain of 705 mg/dm^2 for Curve 3 of Figure 5, before this temperature would be exceeded. On the other hand, a PWR fuel element would reach the same corrosion level after 270 days of operation with a fouling coefficient of 2900 Btu/hr x ft^2 x ^{o}F. (See Curve 1 of Figure 5). For a maximum surface temperature of 680^{o}F and the same heat flux, a fouling coefficient of 4,200 Btu/hr x ft^2 x ^{o}F could be tolerated for the same corrosion time and weight gain.

C. Surface Boiling Considerations

Bubble formation at the surface of the fuel element could have two opposing effects with respect to the postulated mechanisms of heat transfer corrosion. If deposits on the cladding are blown off with surface boiling, lower metal/oxide interfacial temperatures would result. On the other hand, if higher corrosion rates are experienced with surface boiling, the postulated mechanism would result in a more serious case. Accordingly, considerations of surface boiling in the reactor core, especially at high heat fluxes and temperatures, would require long time heat through-put mock-ups to determine the heat transfer corrosion under these conditions.

D. Limitations on Results

The following limitations must be considered in applying the previous results:

(1) The basic mechanism of heat transfer corrosion utilized assumes no flaking of the oxide. Some testing at high temperatures indicated flaking for weight gains approaching 1000 mg/dm^2 [2]. Limitations on corrosion due to release of significant quantities of induced activity in Zr have not been determined. It is possible that the maximum permissible value would be reached before the flaking occurred.

(2) Breakaway corrosion rates at temperatures greater than 750°F are extrapolated from the data shown in Figure 1.

(3) The thermal conductivity of corroded zircaloy was determined from test data submitted by the Babcock and Wilcox Co. . Limitations on the value (0.79 Btu/hr x ft^2/ft x °F) chosen for this analysis are presented in the Appendix. A change in thermal conductivity would be directly reflected in the heat transfer corrosion analysis presented herein as though a proportional change in heat flux were effected. Hence, if the lower confidence limit of 0.52 Btu/hr x ft^2 (see appendix) were utilized in the analysis, the effect on the curves presented in Figures 2, 3, and 4 would be equivalent to an increase in heat flux to approximately 1.5 times the original value. Accordingly, interpolation between the curves calculated for varying heat fluxes with constant surface temperature would correspond to the graphic representation of the lower confidence limit on the mean. As will be shown in the appendix, it was felt that the mean is more significant in the analysis. The general conclusions presented in the report would not be modified if the lower confidence limit is chosen as a basis for analysis but some of the absolute parameters given in the discussion would be changed accordingly. For example, for a scale thickness of 1.8 mils, Curve A indicates a corrosion time after breakaway of about 1675 days as opposed to 1435 days for the case of a curve based on the lower confidence limit. The difference between the two curves decreases with decreasing time as might be predicted from the interpolation suggested above.

(4) Surface boiling as discussed under C above may either minimize or accentuate the heat transfer corrosion problem.

(5) Possible effects due to irradiation have not been taken into consideration.

E. Summary and Conclusions

Subject to the limitations noted above, heat transfer corrosion does not pose a problem for PWR reference designs. Indeed, heavy fouling also would cause no corrosion problems, but the increased temperatures of the fuel element would be undesirable in PWR. This analyses of course, makes no allowance for the effect of fouling on flow characteristics. As soon as pertinent data on the corrosion resistance of U-Mo alloys at the temperature of the core-cladding interface are more firmly established, the quantitative effect of these higher temperatures will be determined.

Appendix

Heat Transfer Properties of Corroded Zircaloy

I. Introduction

Under subcontract 14-302[2], the Babcock and Wilcox Company conducted tests to determine the thermal resistance of corroded zircaloy plates. The results are summarized and evaluated below.

II. Test Procedure and Calculations

The test section consisted essentially of a heat exchanger in which a zircaloy flat plate (4" x 8" x 1/32") was clamped between two rectangular flanges. Heat was transferred through the plate from hot water flowing countercurrently to the cold circuit coolant. Inlet and outlet temperature measurements and flow data were used to calculate overall heat transfer coefficients.

The plates were tested clean, then corroded in static autoclaves, and finally retested in the corroded condition. Accordingly, the data resulted in an overall heat transfer coefficient for each plate tested, both before and after corrosion. With constant film coefficients on both the hot and cold sides, the heat transfer parameter (δ/ks) may be determined:

(12)

$$U_1 = \frac{1}{\frac{1}{h_1} + \frac{1}{h_2} + \frac{(L)}{(k)_p}}$$

$$U_2 = \frac{1}{\frac{1}{h_1} + \frac{1}{h_2} + \frac{(L)}{(k)_p} + \frac{2(\delta)}{(k)_s}}$$

$$(13) \quad \frac{1}{U_1} - \frac{1}{U_2} = \frac{2(\delta)}{(k)_s}$$

where: U_1 = overall heat transfer coefficient for the clean plate, Btu/hr x ft^2 x °F

U_2 = overall heat transfer coefficient for the corroded plate, Btu/hr x ft^2 x °F

h_1 = film coefficient for hot circuit

h_2 = film coefficient for cold circuit

$\frac{(\delta)}{(k)_s} = \frac{\text{Thickness of scale per plate side}}{\text{Thermal conductivity of scale}}$

$\frac{(L)}{(k)_p} = \frac{\text{Plate Thickness}}{\text{Thermal conductivity of plate}}$

Equation (13) holds only for the case where the film coefficient on the hot and cold sides are constant. Since the velocities in each circuit were constant, any possible change in the film coefficients would be attributed to surface roughing effects due to the scale. Accordingly, Wilson plots were made both before and after the specimens were corroded and film coefficients for each case determined. Since no significant changes in the film coefficients were detected, equation (17), is substantiated. It should be noted that a variation in thickness among machined plates required difference measurements on individual plates. This difference in thickness accounts for some of the variation in the clean coefficients shown in Tables 4 and 5, under Results, Section III. As will be noted later, standardization to common weight or thickness bases resulted in equivalent coefficients within the error of the experiment.

$\frac{(\delta)}{(k)_s}$ values obtained for varying corrosion levels are summarized in Tables 4 and 5. The assumption is made here that the thermal conductivity of zircaloy scale is not temperature dependent. Constant thermal conductivities over large temperature ranges have been determined for both stabilized zirconium oxide[8] and zircaloy. The average measurement temperature in the Babcock and Wilcox test was approximately 220°F (350°F hot side and 90°F for the cold circuit).

Considerable scatter in the data was noted upon attempting to correlate $\frac{(\delta)}{(k)_s}$ with weight changes. Accordingly, the data was analyzed in the following fashion.

Assuming a density of 5.6[9] for the scale, equation (9) was derived as shown on page 11:

$$(9) \quad \delta = 0.225 \times 10^{-6} \quad w$$

where δ = thickness in feet

w = weight gain in mg/dm^2

Also, from the data, a correlation independent of the scale thickness may be obtained:

$$(14) \quad w = c \quad \frac{(\delta)}{(k)_s}$$

where c = constant

From (9) and (14), the thermal conductivity of the scale was determined.

In order to achieve thick films within the available time, steam corrosion at 750°F (1500 psi) was used for nine of the plates. Accordingly, the data was analyzed to detect differences between the thermal properties of the scales due to their formation in liquid or steam phases.

For purposes of testing whether or not the thermal conductivities of the scales formed by the two exposures actually differed, a logarithmic normality assumption is necessary. Plots of the data in Figures 6 and 7 show the approximation to a logarithmic normal distribution. The transformation resulted in a 3% probability of obtaining a more extreme difference than the one found if the population means actually do not differ. Accordingly, if one accepts the 5% dividing line between significance and non-significance commonly suggested[10], a difference between the k values is indicated. However, it was decided that the arithmetic mean* of the conductivities of the scale formed by exposure to 680°F water be used in the previous analysis. This choice was made in order to use the more pessimistic value.

From Babcock and Wilcox data [11], an estimate of the experimental error for a single plate was obtained, corresponding to a standard deviation of 41 Btu/hr x ft^2 x °F in the overall heat transfer coefficient. As mentioned previously, the clean overall coefficients should differ due to a variation in thickness among plates. Accordingly, it might be expected that, upon correcting the plates to a standard weight or thickness basis, the clean overall coefficients should agree within the error of the experiment. Babcock & Wilcox Progress Report No. 5076 shows a -8% to +12% variation from the mean in the corrected coefficients for the clean plates after subtraction of the film coefficients. This variation is about twice that which would be found for the measured clean overall heat transfer coefficients. Examination of the data for the corresponding standardized

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* This value, corresponding to the minimum root mean square deviation, is the best estimate of the population mean. As will be shown later, this value is applicable to general calculations for the reactor core in service.

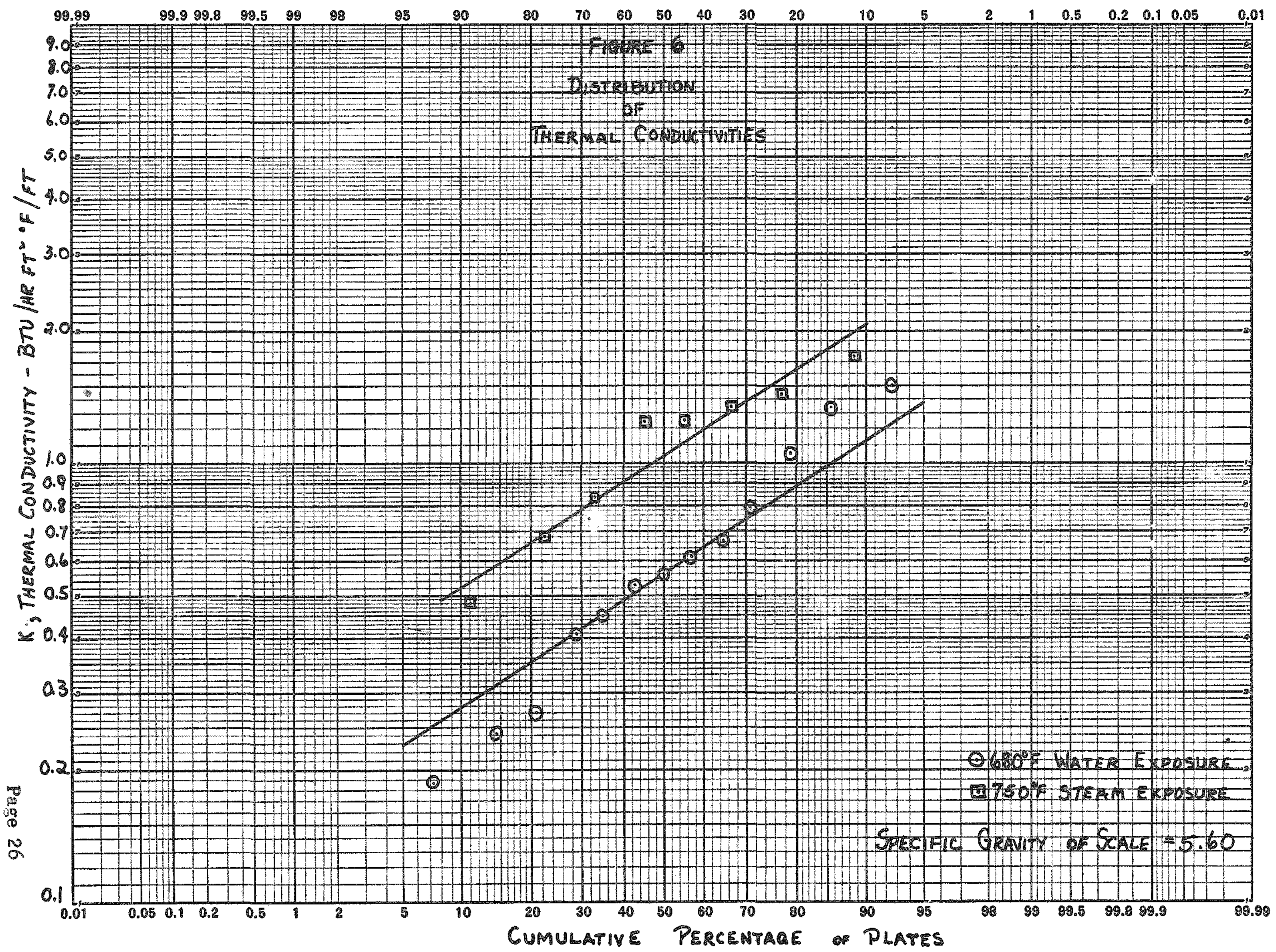

FIGURE 6

DISTRIBUTION OF THERMAL CONDUCTIVITIES

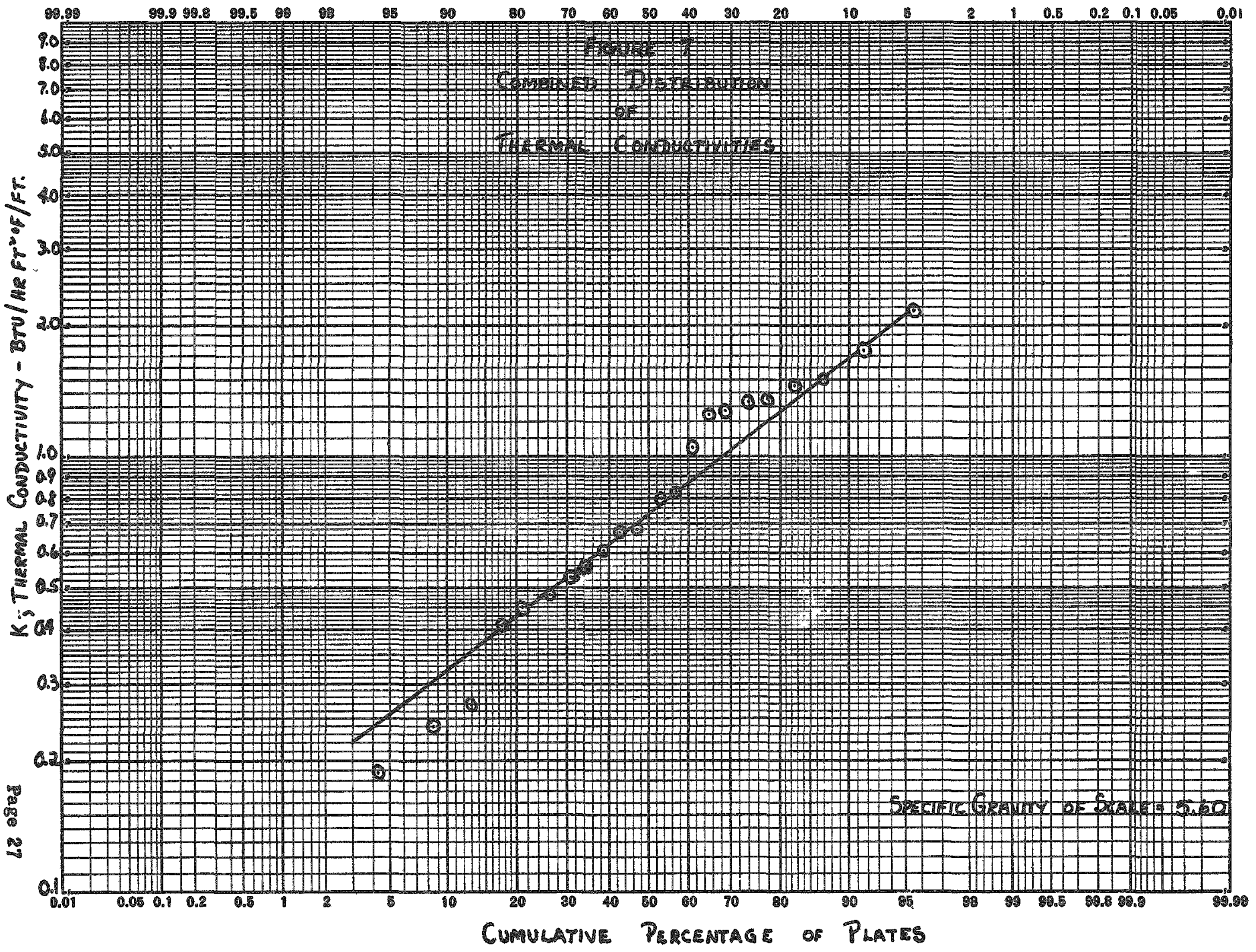

FIGURE 7

COMBINED DISTRIBUTION OF THERMAL CONDUCTIVITIES

SPECIFIC GRAVITY OF SCALE = 5.60

overall heat transfer coefficients reveals a standard deviation of 43 Btu/hr x ft^2 x °F as compared to 41 Btu/hr x ft^2 x °F found in the test of reproducibility, thus indicating that the variance found for the corrected clean coefficients was due to experimental error and not to a difference in properties among plates. Likewise, upon correcting the calculated scale factors to a standard weight gain, the corresponding thermal conductivities should agree within the error of the experiment provided that there is no difference in properties among the corroded plates. A variance of 58 Btu/hr x ft^2 x °F was found in the overall coefficients corresponding to the standardized fouling factors of the plates exposed to 680°F water.

Since,

$$(15) \qquad \sigma_T^2 = \sigma_K^2 + \sigma_{E_1}^2 + \sigma_{E_2}^2$$

where σ_T^2 = total variance for samples exposed to 680°F water

$\sigma_{E_1}^2$ = variance due to experimental error in clean overall coefficients

$\sigma_{E_2}^2$ = variance due to experimental error in overall coefficients for corroded plates

σ_K^2 = unknown variance of standardized coefficients due to difference in physical or chemical properties

it can be seen that the variance observed in the data must be attributed to experimental error and not to differences in properties of the scale or plates.

$$(58)^2 = \sigma_K^2 + (41)^2 + (43)^2, \therefore \sigma_K^2 \cong 0$$

In conclusion, the calculated conductivities presented in this report may be utilized in general reactor core calculations. Deviations from the arithmetic mean are attributed to statistical scatter in measurements and do not represent extreme values of the thermal conductivity of zircaloy scale which might occur in a given core containing a zircaloy 2 heat transfer surface.

III. Results

Table 3

Calculated Thermal Conductivities

	k_s, Btu/hr x ft^2 x °F/ft
1. Mean thermal conductivity of zircaloy scale formed by steam exposure (750°F, 1500 psi)	1.24
k_s, 95% limits*	0.78 - 1.65
2. Mean thermal conductivity of zircaloy scale formed by water exposure	0.79**
k_s, 95% limits*	0.52 - 1.21
3. Mean of combined results	0.97

4. *** General relationship based on mean fouling coefficient corresponding to 2.

$$w = 3.5 \times 10^6 \frac{(\delta)}{(k)_s}$$

where w = weight gain in mg/dm^2

$1/\frac{(\delta)}{(k)_s}$ = heat transfer coefficient of scale, Btu/hr x ft^2 x °F

---

* log normal distribution

** The value of 0.79 Btu/hr x ft^2 x °F/ft was used in the heat transfer corrosion analysis presented in the report.

*** This relationship is independent of the scale density. 1 thru 3 are based on a specific gravity of 5.6 for the scale.

Table 4

Summary of Data and Calculated Conductivities for Zircaloy 2 Plates Exposed to 750°F Steam

Plate #	U_1	U_2	$2\left(\frac{\delta}{k}\right)_s \times 10^4$	$U_s \times 10^{-4}$	w	k_s
6881	2263	2194	0.139	14.39	21	0.680
6887	2102	2063	0.090	22.22	25	1.25
6889	2099	2046	0.123	16.20	34	1.24
6890	2306	2150	0.315	6.35	123	1.76
6892	2051	2003	0.117	17.10	37	1.42
6894	2086	2052	0.070	28.61	34	2.19
6898	2032	1853	0.475	4.21	88	0.832
6902	2109	1958	0.365	5.47	40	0.480
6903	2095	1864	0.592	3.38	174	1.32

U_1 = overall heat transfer coefficient of clean plate, Btu/hr x ft^2 x°F

U_2 = overall heat transfer coefficient of corroded plate, Btu/hr x ft^2 x °F

$\frac{(k)}{(\delta)_s} = U_s$ = Heat transfer coefficient of zircaloy scale, Btu/hr x ft^2 x °F

w = weight gain of corroded plates, mg/dm^2

k_s = thermal conductivity of scale, Btu/hr x ft^2 x °F/ft

Table 5

Summary of Data and Calculated Conductivities for Zircaloy 2 Plates Exposed to 680°F Water

Plate #	U_1	U_2	$\frac{2(\delta) \times 10^4}{(k)_s}$	$U_s \times 10^{-4}$	w	k_s
6335 a)	2240	2065	0.383	5.22	16	0.188
6335 b)	2240	2083	0.336	5.96	18	0.240
6336 a)	2257	2193	0.129	6.75	15	0.524
6336 b)	2257	2127	0.270	7.41	27	0.450
6879	2028	1993	0.087	22.99	26	1.34
6880	2077	2009	0.163	12.27	24	0.662
6884	2061	1996	0.158	12.66	28	0.798
6885	2046	1950	0.241	8.31	30	0.560
6888	2050	1895	0.399	5.01	24	0.270
6893	2031	1964	0.168	11.91	23	0.616
6900	2014	1993	0.052	38.04	29	2.50
6901	2042	2014	0.068	29.40	23	1.50
6904	2124	2079	0.102	19.63	24	1.06
6905	2108	1947	0.392	5.10	25	0.402

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