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MEMORANDUM FOR: B. C. Rusche, Director
Office of Nuclear Reactor Regulation

R. B. Minogue, Director
Office of Standards Development

FROM: S. Levine, Director
Office of Nuclear Regulatory Research

SUBJECT: RESEARCH INFORMATON LETTER-9, HIGH TEMPERATURE OXIDATION OF ZIRCALOY FUEL CLADDING IN STEAM

This memorandum transmits the results of completed research on the high temperature oxidation of Zircaloy fuel cladding in steam. This research is applicable to ECCS performance calculations for light water reactors fueled with U-235. The technical summary given in Enclosure 1 presents the major findings of the work completed to date. The enclosed reports (Enclosures 2-8) are the pertinent quarterly progress and topical reports published during the conduct of the research. A final report on the isothermal and transient oxidation data is scheduled to be published in March, 1977.

The principal results are the following:

1. The new data on the isothermal oxidation rate of Zircaloy cladding in steam show a rate constant at 2200°F that is only 58% of that of the Baker-Just equation, producing 76% of the oxidation that is calculated with the Baker-Just equation. Contaminants in the steam such as hydrogen, nitrogen, and oxygen (from air intruding during a LOCA) were found to have no significant effects on the oxidaton behavior. No observable effects of steam flow rates were found over the range from 1 to 90 ft/sec. Particular attention was paid to the problem of precise measurements of oxidation rates and reaction temperatures. Rate measurements were made for total oxygen consumed, and for growth of the oxide and oxygen stabilized alpha phase layers formed on the surface during the oxidation. Statistical error analyses were made of the rate data, and absolute error analyses made on the temperature measurements, producing the best characterized, reliable, and accurate oxidation rate data yet determined on Zircaloy in steam.

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2. Transient oxidation experiments were conducted in steam using transient time-temperature histories for postulated LOCA's. The experimentally determined isothermal oxidation rate data were then used in a computer code to calculate the oxidation expected during the experimental transient tests. The experimental results agreed with those predicted by the code, thus verifying the use of the isothermal rate data in calculating the amount of oxidation during postulated reactor accidents.

3. An auto-catalytic reaction of the specimens was not observed in any experiment, though unoxidized specimens were heated in flowing steam from about 400°F to as high as 2732°F in as little as ten seconds, and in a few cases were plunged in a fraction of a second into flowing steam in a furnace held at 2000°F. Some specimen heating above the desired reaction temperature was observed, but each specimen quickly cooled to the reaction temperature and ignition did not occur.

4. The rate of diffusion of oxygen in Zircaloy at high temperatures (beta phase) was found to be approximately one-half that previously reported in the literature and used at this time in best estimate and evaluation model calculations of embrittlement of fuel cladding during a postulated LOCA. Particular attention was paid to the problems of measurements of diffusion rates and temperatures. Three independent methods of determination were used in the diffusivity study. The excellent agreement of the data from the three independent methods, as shown in Reference 6, indicates that the new data are free from systematic errors.

Evaluation and Applicability

1. This program and its results have been reviewed repeatedly while in progress by the Zircaloy Cladding Review Group at quarterly Zircaloy Cladding Program Review meetings and at the Annual Water Reactor Safety Research Information Meetings. Interested vendors, public, and scientists from other organizations have attended both. The quarterly and topical reports issued have received RPC-3 distribution (32? copies) and have been obtained from NTIS by numerous researchers in both this and other countries. The consensus has been that the work has been conducted competently and with sufficient attention to technical detail, precision, and accuracy. Extreme care was taken to eliminate the uncertainties in temperature measurement characteristic of the data previously reported. The new oxidation rate data have been confirmed by more limited studies in Japan and Germany.

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2. The impact of the new data on LOCA analyses was examined by calculating peak cladding temperatures using both the new data and the Baker-Just correlation in a FRAP-T3:RELAP-4 computer code simulation of an experimental LOCA test conducted several years ago. At calculated cladding temperatures near 2200°F, the new equation predicts a temperature 133°F lower than that predicted using the Baker-Just correlation.

3. The reduced rate of heat generation as calculated using the new data, along with the experimental observations, indicate only a small probability of possible ignition of the fuel cladding during a LOCA. In addition, the experiments indicate that the oxide film formed on the fuel rods by corrosion during normal operation should cause a significant decrease in the total oxidation occurring during a postulated accident from that calculated using unoxidized fuel cladding.

4. It was observed that an additional conservatism may sometimes occur in the application of the isothermal rate data to LOCA calculations. In instances where (a) the first temperature peak in the LOCA is greater than about 1800°F, (b) the following temperature minimum is less than about 1500°F, and (c) the second temperature peak is less than about 2200°F, the experimentally observed consumption of oxygen is significantly less than that calculated using the isothermal rate data, as is the thickness of the oxide film. However, the thickness of the oxygen stabilized alpha layer appears to be increased almost as much as the thickness of the oxide layer is decreased, so that the thickness of ductile wall left to sustain loads is almost unchanged. It is thought that the "anomalous oxidation effect" is due to a recently discovered hysteresis in the phase transformations of the oxide film at temperatures between about 1600 and 2200°F.

5. The present ECCS Acceptance Criteria place the limitations of 2200°F peak cladding temperature and 17% equivalent oxidation of the wall thickness to limit the degree of embrittlement of the fuel cladding during and after a LOCA. Evaluation models frequently use the present literature data on the diffusivity of oxygen in beta phase Zircaloy, in addition to the thicknesses of oxide and oxygen stabilized alpha phase calculated, to estimate the depth of oxygen penetration into the beta phase from the alpha-beta interface. They then estimate the wall thickness of ductile wall remaining to sustain loads imposed during and after reflooding of the core. The new diffusivity data indicate that there would be significantly less depth of embrittlement in the fuel cladding wall calculated for any given postulated accident, and more wall

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left capable of sustaining loads later in the accident sequence. This, combined with the rate data determined on the growth of oxide and oxygen stabilized alpha layers, will produce a more scientific base for establishing embrittlement criteria for ECCS Acceptance Criteria.

These results have been obtained in response to the specific directive given RES by the Commissioners to obtain new, better, and better-characterized data on the oxidation rate of Zircaloy in steam. They confirm that there is a large degree of conservatism in the evaluation model being used by the Regulatory Staff for calculating the oxidation of Zircaloy during a LOCA. RES will be happy to furnish you any cooperation and assistance that you may require in planning for a change in the ECCS acceptance criteria in 10 CFR 50 Appendix K.

Original Signed by
Saul Levine
Saul Levine, Director
Office of Nuclear Regulatory Research

See next page.

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Enclosures:

1. Appendix 1: Technical Summary - High Temperature Oxidation of Zircaloy Fuel Cladding in Steam
2. J. V. Cathcart, Quarterly Progress Report on the Zirconium Metal-Water Oxidation Kinetics Program Sponsored by the NRC Division of Reactor Safety Research for January-March 1976, ORNL/NUREG/TM-17, May 1976
3. J. V. Cathcart, Quarterly Progress Report on the Zirconium Metal-Water Oxidation Kinetics Program Sponsored by the NRC Division of Reactor Safety Research for April-June 1976, ORNL/NUREG/TM-41, August 1976
4. J. V. Cathcart, Quarterly Progress Report on the Zirconium Metal-Water Oxidation Kinetics Program Sponsored by the NRC Division of Reactor Safety Research for July-September 1976, ORNL/NUREG/TM-62, December 1976
5. J. V. Cathcart, et. al., Zirconium Metal-Water Oxidation Kinetics I. Thermometry, ORNL-5102, February 1976
6. R. A. Perkins, Zirconium Metal-Water Oxidation Kinetics II. Oxygen-18 Diffusion in Beta Zircaloy, ORNL/NUREG/TM-19, July 1976
7. R. E. Pawel, Zirconium Metal-Water Oxidation Kinetics III. Oxygen Diffusion in Oxide and Alpha Zircaloy Phases, ORNL/NUREG-5, October 1976
8. S. Malang, SIMTRAN I - A Computer Code for the Simultaneous Calculation of Oxygen Distributions and Temperature Profiles in Zircaloy During Exposure to High-Temperature Oxidizing Environments, ORNL-5083, November 1975

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cc w/Enclosure 1:
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ENCLOSURE

TECHNICAL SUMMARY

HIGH TEMPERATURE OXIDATION OF ZIRCALOY FUEL CLADDING IN STEAM

This summary transmits part of the new information obtained in an RES-sponsored research program on the rate of oxidation of Zircaloy fuel cladding in steam and the rate of diffusion of oxygen in beta phase Zircaloy. We believe the new data should allow quantification of the conservatism of the required use of the Baker-Just rate constant equation for calculation of the rates of oxidation of Zircaloy, as stated (Ref. 1) in the present ECCS Acceptance Criteria.

In Docket No. RM-50-1, Acceptance Criteria for ECCS in LWP, the Commissioners of the AEC stated (Ref. 2):

> "This equation was derived by Baker and Just from their measurement of the rate of oxidation at the melting point of zirconium, in conjunction with Lemmon's and Bostrom's data at lower temperatures. The equation is a straight line representation of a plot of the logarithm of the reaction rate vs. the reciprocal of the absolute temperature. The slope of this line is the activation energy, and depends in an important way on the single point of Baker and Just at the melting point of zirconium."
>
> "The Baker-Just equation has been criticized extensively, ...
>
> "Until new data are obtained and present doubts are resolved we believe it best to continue the use of the Baker-Just equation."
>
> "There is evident need for new and better experimental data to resolve this issue and to provide a rate equation with a more representative activation energy...."

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They also directed (Ref. 3) "...the Director of the Division of Reactor Safety Research to give priority attention to study to determine more exactly the temperature at which clad embrittlement ceases to be simply a function of oxidation". A confirmatory research program sponsored by RES and nearing completion at ORNL has provided new data and rate equations pertinent to these needs.

The principal results are as follows:

1. The rate constant[(a)], δ_T, for total oxygen consumed during the isothermal oxidation of Zircaloy-4 in steam at atmospheric pressure has the temperature dependence from 1832°F to 2732°F (Ref. 4,5)

$$\delta_T^2/2 = 0.1811 \quad \exp[-39{,}940/RT] \quad (g/cm^2)^2/s.$$

   For comparison, the Baker-Just equation (Ref. 6) in the same units is

$$\delta_T^2/2 = 2.0496 \quad \exp[-45{,}500/RT] \quad (g/cm^2)^2/s.$$

   Equations of the same form have been developed (Ref. 4,5) for the thicknesses of the oxygen-stabilized alpha layer, the oxide layer and the Xi layer[(b)]. The new data are reported graphically in Figure 1.

2. The diffusivity of oxygen in beta phase Zircaloy-4 was found (Ref. 7) to have the temperature dependence from 1832°F to 2732°F

$$D = 2.63 \times 10^{-2} \quad \exp[-28{,}200/RT] \quad cm^2/s \text{ for oxygen-16.}$$

   The values of the diffusivity of oxygen in this temperature range are approximately one-half those reported previously for Zircaloy-2 by Mallett, et. al. (Ref. 8). and now used for calculating the oxygen gradients in the beta phase of oxidizing cladding. The data are compared in Figure 2.

(a) for the parabolic rate equation $W = \delta\sqrt{t}$, with W = grams of oxygen consumed, t = seconds, and δ = the parabolic rate constant.

(b) the Xi layer thickness is the sum of the oxide and alpha layer thickness.

3. Two computer codes, SIMTRAN-I (Ref. 9) and BILD-5 (Ref. 10) have been written for calculating total oxygen consumed, alpha and oxide layer thicknesses, and the distribution of oxygen in the beta phase during postulated temperature transients. SIMTRAN-I will also calculate temperature distributions in the fuel cladding during the temperature transients, but it requires more time to run. Both codes have been verified with experimental data obtained in transient temperature oxidation experiments at ORNL.

The new oxidation rate data are compared in Figure 3 with the Baker-Just (B-J) rate equation and with data recently reported by other investigators. At 2200°F, the new data show a rate constant for oxidation 58% of that calculated by the B-J equation. The new ORNL data have been essentially confirmed by data recently reported by Kawasaki (Ref. 11,12) and by Leistikow (Ref. 13) and the disagreement with the B-J correlation confirmed by data reported by Heidrick (Ref. 14) and by Biederman (WPI) et. al. (Ref. 15). The new data also agree quite well (Figure 4) with the oxidation data reported by Hobson and Rittenhouse (Ref. 16) as recalculated by Pawel and Hobson (Ref. 17).

Extreme care was taken in all experiments to be certain of the accuracies of the temperature measurements and to allow the conduct of statistical evaluations of the experimental data. The absolute errors in temperature measurements were within ±7.2°F at 1652°F and within ±10.8°F at 2732°F. The 90% confidence intervals[(c)] for the rate constant $\delta^2/2$ as calculated by the new rate equation are ±3.3% at 1922°F, ±1.7% at 2192°F and ±2.9% at 2732°F. Admission of 5% hydrogen, 10% nitrogen, or 10% oxygen to the flowing steam had no definitely measurable effect on the oxidation rates. Steam flow velocities from about 1 ft/sec to about 90 ft/sec had no observable effect.

An experimental simulated LOCA test, FRF-2 (Ref. 18), has been modeled using FRAP-T3 and RELAP-4. Calculations were made of peak cladding temperatures and total oxygen consumed using the B-J correlation and then repeated with the new Cathcart-Pawel (C-P) correlation substituted for the B-J equation (Ref. 19). These values were then used to estimate the thicknesses of the oxide and oxygen-stabilized

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(c) The physical significance of the 90% confidence interval is that if the experimental data were redetermined under the same conditions by the same techniques as that reported, there is a 90% probability that the best estimate line for the new data would lie inside the intervals specified.

alpha layers, the Xi thickness, and the thickness of beta phase remaining, assuming an original wall thickness of 0.025 inches. The results are given in Table I. At 200 seconds into the calculated LOCA, the peak cladding temperature was 2335°F using the B-J correlation and 2232°F using the C-P equation. The reduction in calculated peak cladding temperature using the new data in this model was approximately 100°F. The wall thicknesses consumed were 10.3% and 6.5%, respectively. While the oxygen profiles in the remaining beta phases were not calculated, the new diffusion data (Ref. 7) show that the depth of contamination would be considerably less (the diffusion rate is approximately one-half that previously reported by Mallett (Ref. 8)).

In the determination of the new diffusion rate data, the absolute temperature errors were within ±1.8°F at 1652°F and ±3.6°F at 2732°F. The 90% confidence intervals for the diffusivity, D, of oxygen in beta phase Zircaloy-4 are +7.8%, -7.2% at 1832°F, +4.2%, -3.9% at 2282°F, and +10.0%, -9.1% at 2732°F. The new data were obtained by both tracer and chemical diffusion data (no statistically significant differences) and the diffusivity was found to be independent of oxygen content in the beta phase.

A final report on these parts of the ORNL study will be issued by March 1977.

REFERENCES

1. 10 CFR 50 Appendix K, Section A.5. Metal-Water Reaction Rate.

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3. Ibid., I. Introduction, p. 10.

4. ORNL/NUREG/TM-41, "Quarterly Progress Report on the Zirconium Metal-Water Oxidation Kinetics program sponsored by the NRC Division of Reactor Safety Research for April-June 1976", August 1976, J. V. Cathcart.

5. "Summary of the Zirconium Metal-Water Oxidation Kinetics Program" J. V. Cathcart, et. al., Fourth Water Reactor Safety Research Information Meeting, September 27-30, 1976, National Bureau of Standards, Gaithersburg, Maryland.

6. ANL-6548, "Studies of Metal-Water Reaction at High Temperature, Part III: Experimental and Theoretical Studies of the Zirconium-Water Reaction" May 1962, L. Baker, Jr. and L. C. Just.

7. ORNL/NUREG/TM-19, "Zirconium Metal-Water Oxidation Kinetics Part II: Oxygen-18 Diffusion in Beta-Zircaloy", July 1976, R. A. Perkins.

8. J. Electrochem Soc. 106: 181-84 (1959) "The Diffusion of Oxygen in Alpha and Beta Zircaloy-2 and Zircaloy-3 at High Temperatures", M. W. Mallett, W. Albrecht, and P. R. Wilson.

9. ORNL-5083, "SIMTRAN I - A Computer Code for the Simultaneous Calculation of Oxygen Distributions and Temperature Profiles in Zircaloy During Exposure to High-Temperature Oxidizing Environments" November 1975, S. Malang.

10. R. E. Pawel, ORNL, unpublished.

11. JAERI-M-6181, "Reaction of Zircaloy Cladding with Steam Under Simulated Loss-of-Coolant Accident Conditions" Saturu Kawasaki, Teruo Furuta and Masao Hashimoto, July 1975.

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12. JAERI-6601 "Zircaloy-Steam Reaction and Embrittlement of Oxidized Zircaloy Cladding in a Simulated Loss-of-Coolant Accident" Teruo Furuta, Satoru Kawasaki, Masao Hashimoto and Takashi Otomo, June 1976.

13. Leistikow, S., GfK, Karlsruhe, FRG, personal communication to J. V. Cathcart, ORNL.

14. Heidrick, T. and Urbanic, V., unpublished AECL data.

15. Biederman, R. R. Third Interim Progress Report, July 1 - September 30, 1975, "A Study of Zircaloy-Steam Oxidation Reaction Kinetics," EPRI Project 249-1, Worcester Polytechnic Institute

16. ORNL-4758, "Embrittlement of Zircaloy Clad Fuel Rods by Steam During LOCA Transients", January 1972, D. O. Hobson and P. L. Rittenhouse.

17. Unpublished, R. E. Pawel and D. O. Hobson, ORNL, 1973, oxidation data recalculated from data originally reported in ORNL-4758 (Ref. 16).

18. Nuclear Technology, Vol. 11, No. 4 (Aug. 1971) pp. 502-520, "Fuel Rod Failure Under Loss-of-Coolant Conditions in TREAT", R. A. Lorenz, D. O. Hobson, and G. W. Parker.

19. Private communication, L. J. Siefkin, INEL (EG&G) to M. L. Picklesimer, NRC, December 16, 1976.

Table I

Calculation[a] of Damage to Cladding During Simulated LOCA Using New and Old Oxidation Correlations

Time into LOCA, sec	25 sec		50 sec		100 sec		150 sec		200 sec	
Correlation Equation[b]	B-J	C-P	B-J	C-P	B-J	C-P	B-J	C-P	B-J	C[illegible]
Peak Cladding Temperature °F	1603	1603	2247	2217	2296	2247	2323	2247	2335	[illegible]12
Thickness of wall consumed, mils	0	0	0.633	0.457	1.50	1.02	2.08	1.38	2.57	1.64
Thickness of wall consumed, %[c]									10.3%	6.55%
Equivalent oxygen consumed, mg O_2/cm^2									13.9	8.9
Estimated oxide layer thickness, mils									2.75	1.72
Estimated alpha layer thickness, mils									2.99	1.87
Estimated Xi layer thickness, mils									5.74	3.5[illegible]
Estimated Xi layer thickness, % wall[c]									22.9	14.4
Estimated thickness of beta Zircaloy remaining, mils									19.3	21.4

(a) Using RELAP-4 and FRAP-T3 modeling of FRF-2 (see Ref. 18)

(b) B-J = Baker-Just correlation
C-P = Cathcart-Pawel correlation (new data)

(c) assuming wall thickness of 0.025 inches

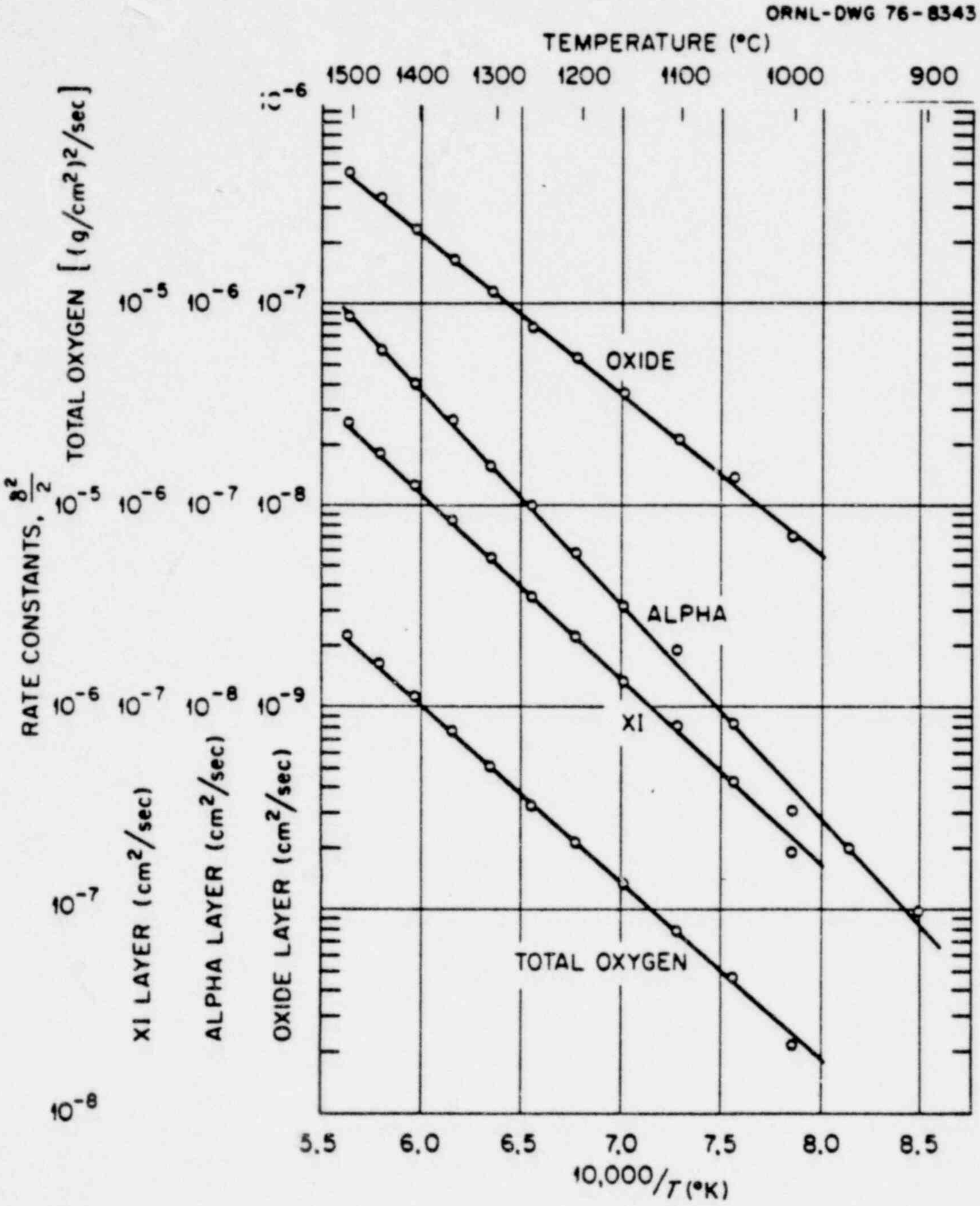

Figure 1. ORNL Experimental Rate Constants for the Oxidation of Zircaloy-4 in Steam.

ORNL-DWG 76-8103

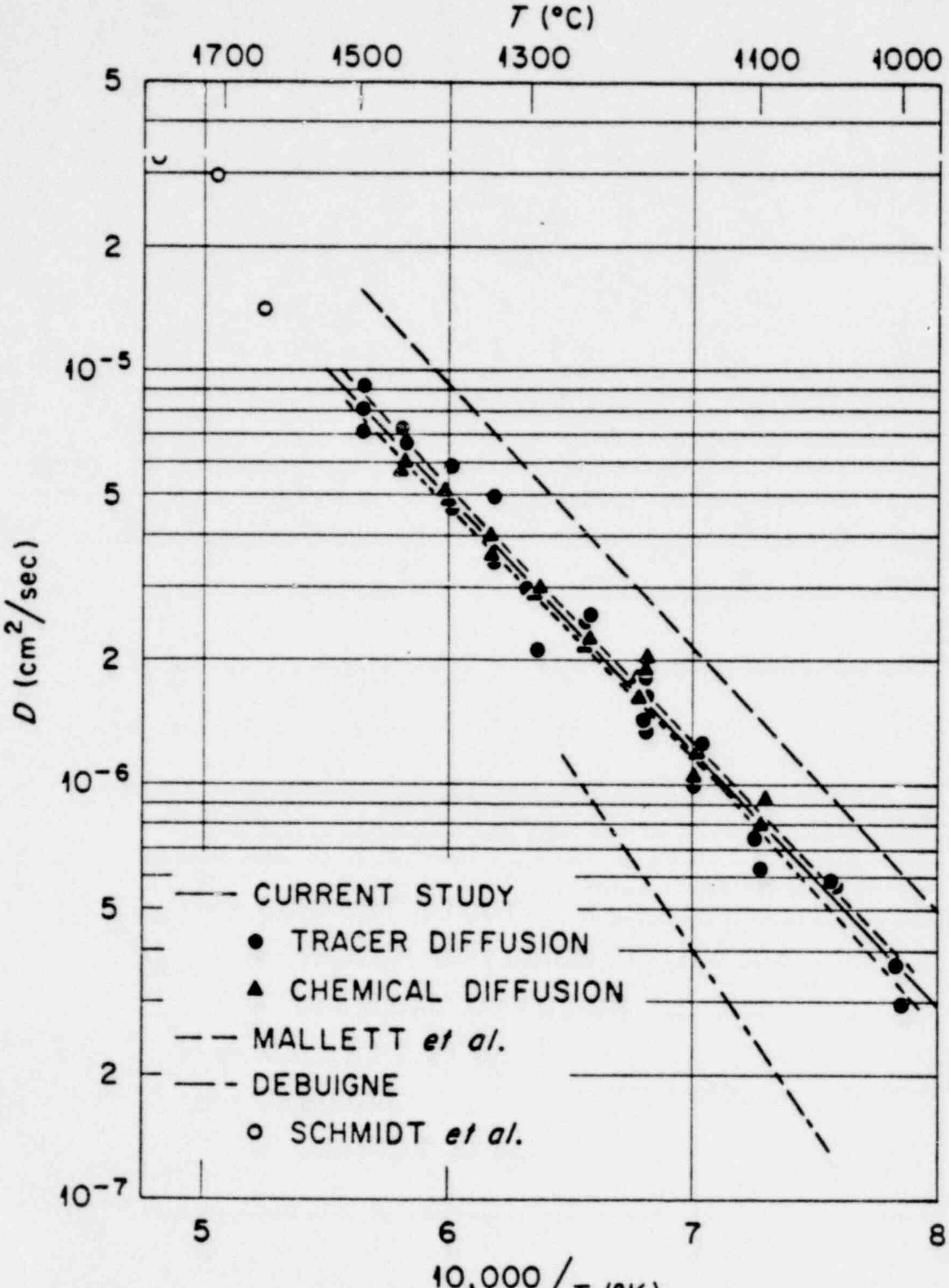

Figure 2. Diffusivity of Oxygen in Beta Phase Zircaloy-4.

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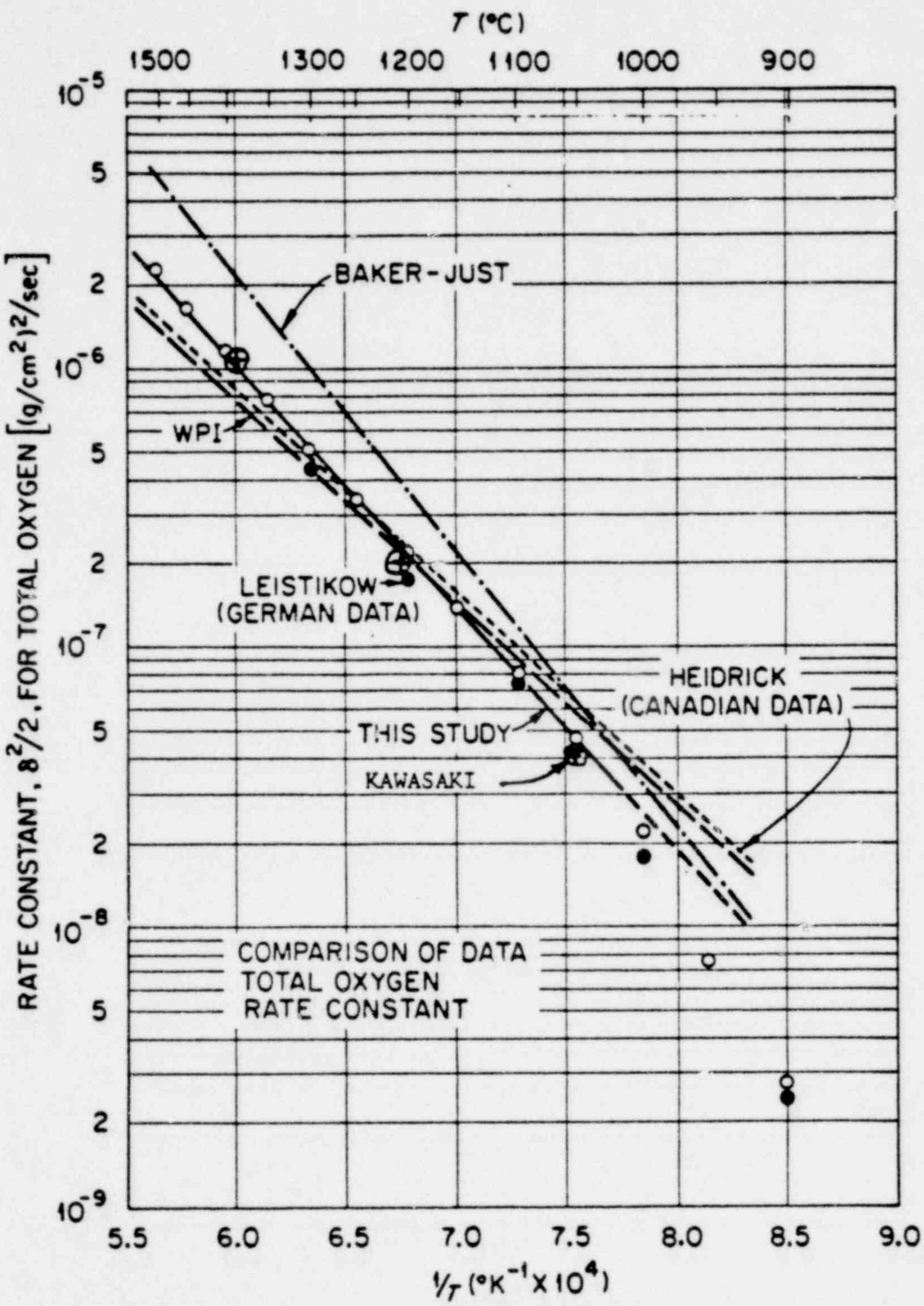

Figure 3. Arrhenius Plot of Oxidation Rate Data for Isothermal Oxidation of Zircaloy-4 in Steam, Total Oxygen Consumed.

ORNL-DWG 76-12344

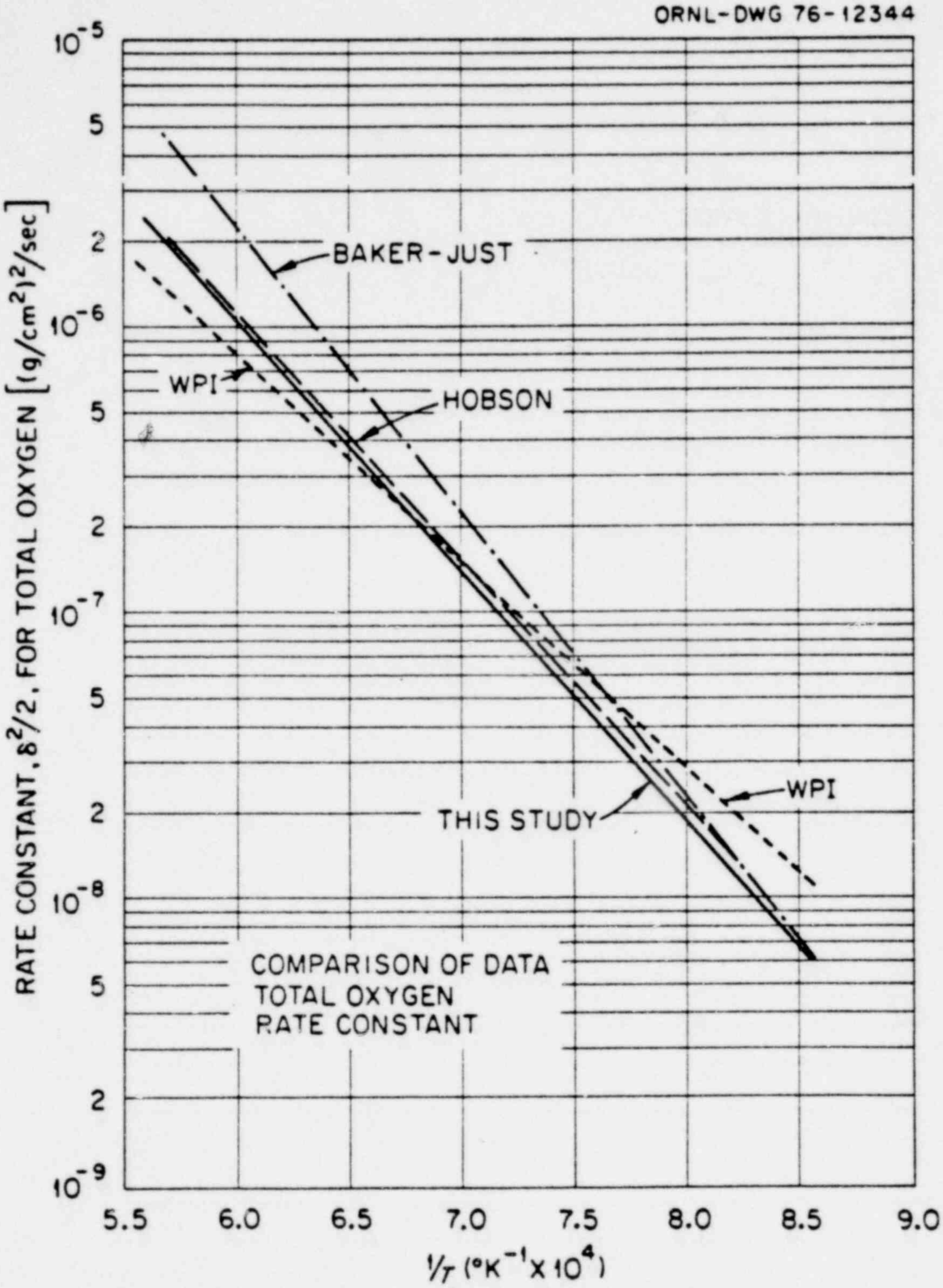

Figure 4. Arrhenius Plot of Isothermal Rate of Oxidation of Zircaloy-4 in Steam, Comparison of Equations.

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