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BROOKHAVEN NATIONAL LABORATORY

MEMORANDUM

DATE: March 27, 1985

TO: K. Perkins

FROM: L. J. Teutonico

SUBJECT: FIN A-3786 - Study of Beyond Design Basis Accidents in Spent Fuel Pools

Two Sandia reports[1,2] deal with the question of rapid zirconium oxidation in a spent fuel pool following loss of water. Both the computer modeling and the experimental simulation, as described in these reports, suggested that in certain fuel racking configurations (a) a self-sustaining zirconium-air oxidation reaction can be initiated, and (b) this self-sustaining reaction can propagate from one region of a pool to another. There are large uncertainties associated with the phenomenology of zircaloy oxidation and its propagation in spent fuel assemblies. This preliminary report on Tasks 3, 4, 5 of the subject FIN (Uncertainities in Oxidation Propagation, SFUELIW Computer Code Validation, Impact of Revised Reaction Rate Equation, respectively) addresses some of these uncertainities and their effects on the initiation and propagation of a self-sustaining zircaloy-air oxidation reaction.

1) The propagation rates of rapid zircaloy clad oxidation in air from the hottest section of the pool (after a loss of water incident) to adjacent sections were estimated (in Ref. 2) under the conditions that the spent fuel in the hottest section of the pool was generating 30 kw/MTU in a room maintained at constant temperature. As pointed out by Han[3], this estimate should be re-calculated under inadequate room ventilation conditions, to simulate properly the conditions at many licensed facilities. Similarly, additional calculations should be performed in which the hot spent fuel decay power is varied from 20 to 90 kw/MTU for both the adequate and inadequate room ventilation conditions. These studies would determine how sensitive the oxidation propagation is to the decay power of the spent fuel stored adjacent to hot fuel, assuming the input oxidation rate data are known with sufficient accuracy.

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2) The above assumes the zircaloy-air reaction rate equation used in the Sandia work is sufficiently accurate. There are a number of uncertainties associated with this equation. We discuss each of these uncertainties in turn.

A. Experimental Data: A literature search [4-147] has revealed that there is a great deal of data for zirconium oxidation; most of it, however, is concerned with oxidation in steam or oxygen. The data for zirconium (zircaloy)-air oxidation presented in Refs. 1 and 2 appear to be the best available. These are shown in Figure 1. The authors (of the SNL reports) fit the data with three separate Arrhenius plots over the temperature range 500-1500°C; one break occurs at the α-β transformation temperature for zirconium, the other at the temperature at which the oxide undergoes a monoclinic-tetragonal transformation. (N.B. two of the sets of data are for zirconium, the other for zircaloy-4). These assumptions are reasonable. It should be noted, however, that there is no a priori reason to expect that the data would be fit by an Arrhenius expression, particularly above the α-β transformation temperature where a number of different processes are occurring simultaneously (discussed further below); therefore the use of the Arrhenius expression should be viewed in this case only as a computational tool. It is difficult to assess the validity of the data employed. What are really required are new experiments to determine the oxidation rate of zircaloy in air over the temperature range of interest, for both isothermal and non-isothermal conditions.

B. Kinetics: The question was raised[2] as to whether the assumption of parabolic kinetics was valid. Data were presented (from Refs. 86 and 126) which show examples of linear as well as cubic kinetics. However, they all apply at temperatures below the α-β transformation temperature. Since almost all rapid oxidation occurs above the α-β transformation temperature, where the oxidation rate is controlled by one or more diffusion processes, the assumption of parabolic kinetics appears to be reasonable.

C. Zirconium vs. Zircaloy: It is assumed in the Sandia work that the oxidation rates of zirconium and zircaloy are essentially the same. Recent work by Pawel and Campbell[136] has shown that this is not the case. Oxidation in steam of both pure zirconium and zircaloy-4 was studied in the temperature range of rapid oxidation (1000°C-1500°C). It was found that at all temperatures the oxidation rate of zircaloy-4 was higher than that of zirconium; the ratio of the two rates is approximately 3 at 1000°C and decreases with increasing temperature to a value of approximately 1.5 at 1500°C (cf. Figure 2). The higher oxidation rate of Zircaloy-4 is attributed to increased oxygen diffusivity in the oxide phase; a lower activation energy was observed, implying that some mechanistic differences exist. Analogous results are expected to apply for oxidation in air.

D. Oxidation Model: The oxidation in steam of both zirconium and zircaloy-4 (in the temperature range 1000-1500°C) is a multi-phase layer process.[136] Not only is an oxide layer formed, but also (beneath it) a layer of oxygen-stabilized α-phase (zirconium or zircaloy). The multi-phase model is only significant above the α-β transformation temperature (approximately 900°C), but this is exactly where rapid oxidation occurs. The parabolic rate constants for oxide layer growth, α-layer growth, and oxygen consumption were determined in Ref. 136 from experimental data and computer modeling. The rate of oxygen consumption is significantly higher at all temperatures than the rate of oxide formation for both zirconium and zircaloy-4. For zirconium the ratio of oxygen consumption rate to oxidation rate is approximately 4 at 1000°C and increases with increasing temperature to a value of approximately 5.4 at 1500°C; for zircaloy-4 the corresponding values are approximately 3.0 and 4.5 at 1000°C and 1500°C, respectively (cf. Figure 2). Although these results were obtained for oxidation in steam, analogous results are again expected for oxidation in air.

E. Effect of Nitrogen: Before discussing the reaction of zirconium with air, let us consider the reaction with nitrogen alone.[148-151] The rate of

reaction of nitrogen with zirconium is much less than the corresponding reaction rate with oxygen; weight gain data[151] after one hour ($800°C<T<1200°C$) indicate that zirconium reacts with nitrogen about 20 times slower than with oxygen. The overall process is very similar to oxidation in view of the high solubility of nitrogen in zirconium, and involves a large amount of dissolution along with film formation. In the case of nitriding in the α-region, a two phase diffusion process describes the behavior whereas β-phase nitriding involves three phases (nitrogen, like oxygen, stabilizes the α-phase, leading to a wide range of α between the nitride and the β-matrix). The reaction product is zirconium nitride (ZrN); the reaction is exothermic, releasing approximately 82 kcal/mole. (The energy released in forming the oxide is approximately 262 kcal/mole.) The thickness of the zirconium nitride layer has been found[149] to be much smaller than that of the dissolution zone (in the temperature range 750°C- 1000°C) which indicates that the rate constant for film formation is considerably smaller than the rate constant for nitrogen dissolution. In fact, at 1000°C, 84% of the total nitrogen uptake was due to dissolution in the metal.

The role of nitrogen in the high temperature reaction of zirconium with air has been investigated[151]. The reaction process is multiphase in nature. Adjacent to the β-phase of the zirconium is a layer of α-phase (stabilized by both oxygen and nitrogen) and a surface layer of ZrO_2. In general, a certain amount of nitride (ZrN) is formed. For temperatures up to approximately 1050°C the nitride is found as a layer between the stabilized α-phase and the oxide layer; above 1050°C the nitride occurs as discrete particles dispersed in the oxide.

It is doubtful whether any appreciable amount of nitride is formed in the problem currently being considered. At the lower temperatures (during heat up) the reaction rate is very slow. Once rapid oxidation is initiated (approximately 900°C) the self-sustaining reaction proceeds very quickly, and

there may not be sufficient time for ZrN to be formed. Any nitride that does form, however, will contribute to the chemical energy release for the self-sustaining reaction.

The reaction rate of zirconium is higher with air than with oxygen alone. The explanation advanced is that nitrogen dissolves in ZrO_2. By replacing oxygen ions in the oxide structure, the higher valency nitrogen can increase the anion vacancy concentration, thus permitting a higher rate of diffusion of oxygen through the anion-deficient zirconia.

In sum, there are a number of uncertainties associated with the zircaloy-air reaction equation. These are particularly important above 900°C where rapid oxidation occurs. The most significant appear to be (i) the difference in the oxidation rates of zirconium and zircaloy, and (ii) the multiphase nature of the oxidation process itself at these temperatures. The results given above in Section C and D (i.e. for zirconium vs. zircaloy-4, and oxygen consumption rate vs. oxidation rate, respectively) apply to oxidation in steam only. Analogous results are expected for oxidation in air, i.e. it is expected that the oxidation rate in zircaloy will be greater than that in zirconium, and the rate of oxygen consumption will be greater than the rate of oxide formation in both materials. The relative magnitude of these effects cannot be deduced from the steam oxidation data. What are required are new experiments and computer modeling (similar to those carried out by Pawel and Campbell[136] for oxidation in steam) for the high temperature reaction of zirconium and zircaloy with air. In lieu of these, we suggest that additional calculations be performed for two other zirconium-air reaction correlations which will serve as bounds for those presented in Figure 1. (a) The high temperature correlation for zirconium (above the phase change of ZrO_2) should be multiplied by a factor m_1 to account for the higher reaction rate in zircaloy. (b) The correlations above the α-β transformation temperature should be divided by a factor m_2 to account for the difference in oxygen consumption rate and rate of oxide formation. Values of m_1 and m_2 as large as five should be considered.

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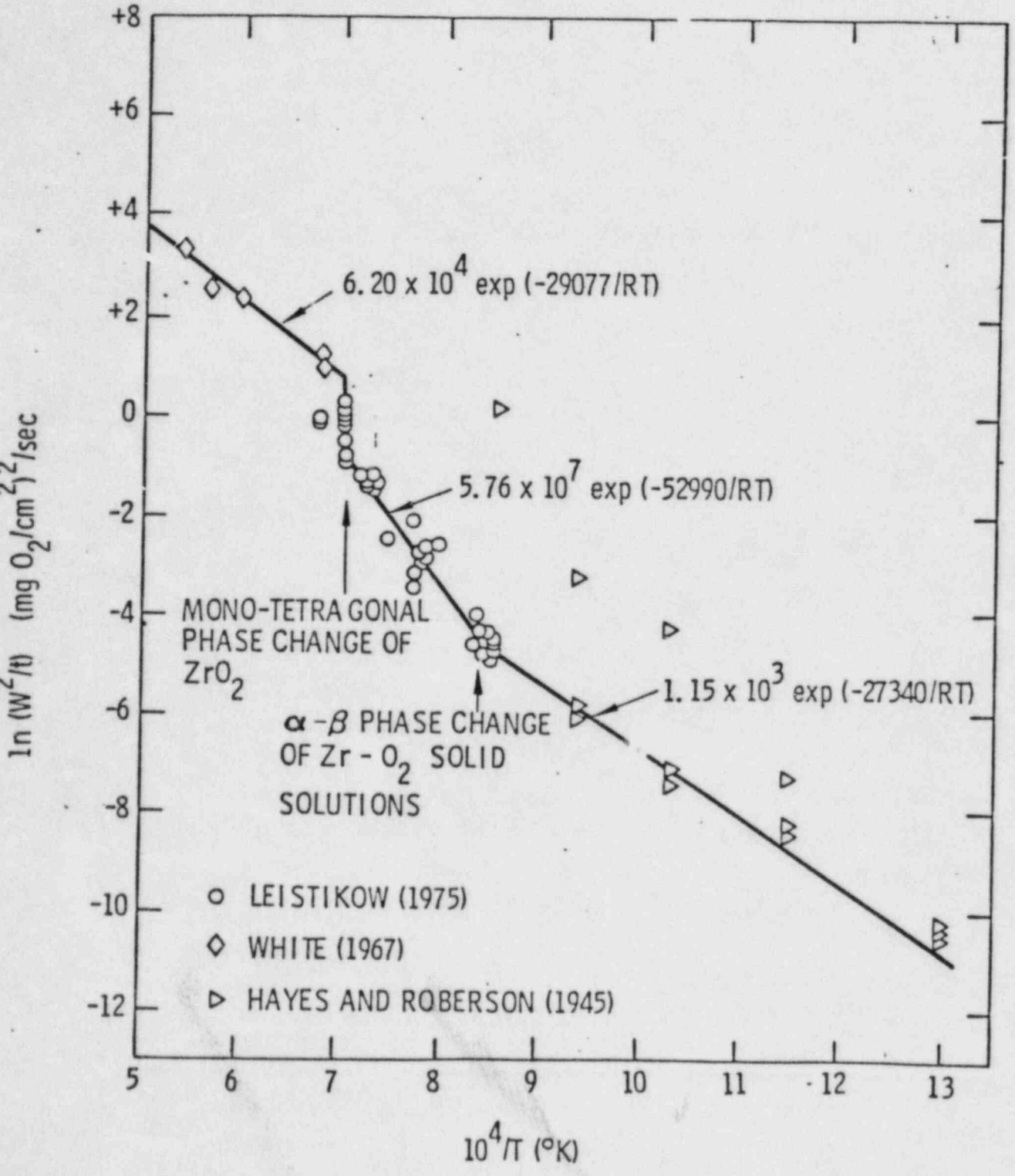

FIGURE 1 CORRELATIONS FOR ZIRCONIUM OXIDATION IN AIR (FROM REF. 1)

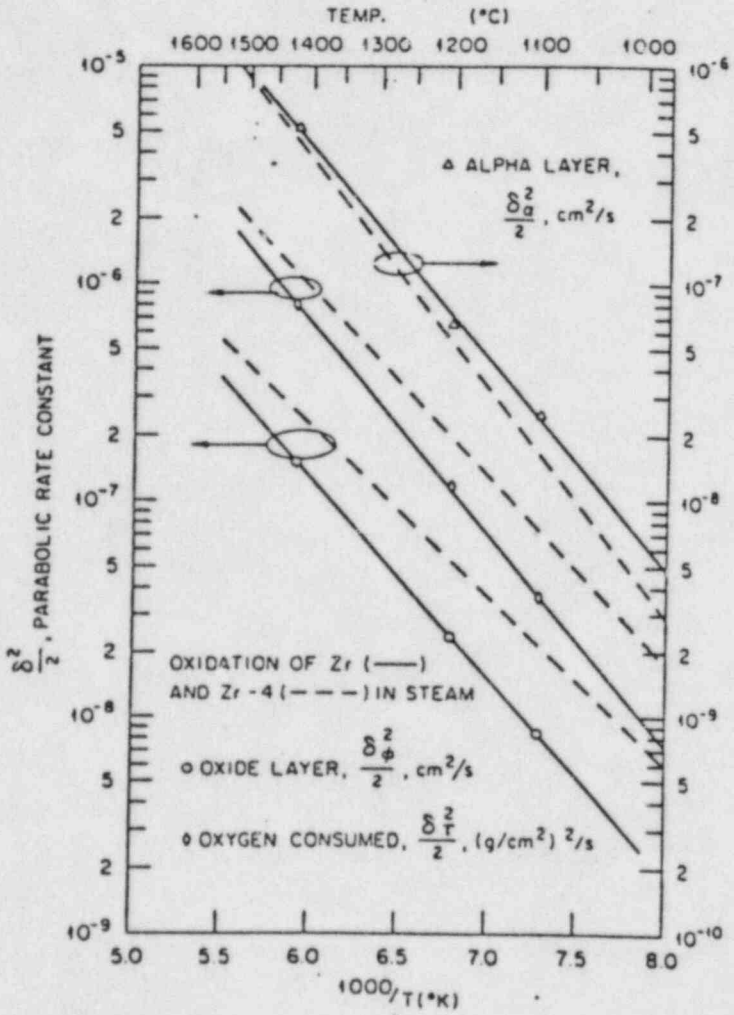

FIGURE 2 PARABOLIC RATE CONSTANTS FOR OXIDE LAYER GROWTH, α-LAYER GROWTH, AND OXYGEN CONSUMPTION FOR THE REACTION OF ZIRCONIUM (SOLID LINES) AND ZIRCALOY-4 (DASHED LINES) WITH STEAM. THE RATE CONSTANTS FOR OXYGEN CONSUMED (WEIGHT GAIN) WERE DETERMINED FROM MODELING ANALYSES (FROM REF. 136).