UNITED STATES
NUCLEAR REGULATORY COMMISSION
WASHINGTON, D. C. 20555

MAY 2 9 1980

Mr. Robert H. Leyse
12525 Saratoga Creek Drive
Saratoga, CA 95070

Dear Mr. Leyse:

In your letter to Commissioner Hendrie, dated April 2, 1980, you stated that Figure 4 of SECY-80-107 was erroneous. The basis for this opinion was your belief that the thermodynamics of the Zircaloy-steam reaction were ignored. In a follow-up telephone discussion with a member of our staff, you stated that, specifically, the peak cladding temperature as displayed in Figure 4 was probably too high. Also, in your letter, you requested that the staff provide you with certain calculations of maximum flame temperature for the zirconium-oxygen and zirconium-water reactions.

The thermodynamics of the zirconium-steam reaction were, in fact, considered in the staff's calculations. The heat of reaction (ΔH_r) was modeled as a constant value of 2808 Btu/lb of zirconium. A more precise temperature dependent ΔH_r could have been used. However, the reaction heat is only a mild function of temperature, decreasing as the temperature increases (Reference 1). Some important thermodynamic limitations were imposed on our calculations. However, these limitations were clearly stated in SECY-80-107. The most important limitation was the assumption of an adiabatic heat-up. This assumption allows no heat to be transferred away from the surface of the rod. This means that enthalphy changes in the gaseous reactants and products (H_2O and H_2) are not considered. Another limitation stated in SECY-80-107 was the assumption that sufficient steam was always available for the reaction. That is, no material balance was made to account for the amount of water consumed or hydrogen produced. Furthermore, it was assumed that the fuel rod's structural integrity would be maintained throughout the transient.

The staff has prepared the enclosed discussion paper addressing the issues identified in your letter. In summary, we find that the calculations performed for SECY-80-107 did consider thermodynamics. The limitations were clearly stated therein. Flame temperature analysis does not provide sufficient information about the relevant processes; specifically, flame temperature analysis ignores the nature of massive zirconium reaction including kinetic effects. The calculations presented in the enclosure show that heat transfer and the presence of other substances (e.g., UO_2) are very important in determining maximum cladding temperatures.

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I trust the information contained in this letter is responsive to the concerns
identified in your letter of April 2, 1980. Mr. Leyse, I thank you for your
interest in these matters and for taking the time to write us about them.

Original Signed by
H. R. Denton

Harold R. Denton, Director
Office of Nuclear Reactor Regulation

Enclosure:
Discussion

Some Thermodynamic Considerations Regarding Zirconium-Water Reactions

The thermodynamics of the zirconium-steam reaction were considered in the staff's calculations. The heat of reaction (ΔH_r) was modeled as a constant value of 2808 Btu/lb of zirconium. A more precise temperature dependent ΔH_r could have been used. However, the reaction heat is only a mild function of temperature, decreasing as the temperature increases (Ref. 1). Some important thermodynamic limitations were imposed on our calculations. However, these limitations were clearly stated in SECY-80-107. The most important limitation was the assumption of an adiabatic heat-up. This assumption allows no heat to be transferred away from the surface of the rod. This means that enthalphy changes in the gaseous reactants and products (H_2O and H_2) are not considered. Another limitation stated in SECY-80-107 was the assumption that sufficient steam was always available for the reaction. That is, no material balance was made to account for the amount of water consumed or hydrogen produced. Furthermore, it was assumed that the fuel rod's structural integrity would be maintained throughout the transient.

Your letter implies that there may be a significant reverse reaction of ZrO_2 and H_2 forming steam and zirconium, and that the equilibrium would be pressure dependent. Since one mol of H_2 forms for each mol of H_2O in the forward reaction, the thermodynamic expression for equilibrium is:

$$\Delta F^0 = - RT \ln \left[\frac{(P_{H_2})^2}{(P_{H_2O})^2} \right]$$

or

$$\exp \left[\frac{-\Delta F^0}{2RT} \right] = K_e = \frac{P_{H_2}}{P_{H_2O}}$$

Where: ΔF^O = standard free energy of reaction

R   = gas cont·nt

T   = absolute temperature

P_{H_2O} = partial pressure of water vapor

Ke = equilibrium constant

P_{H_2} = partial pressure of hydrogen

When solid ZrO_2 is formed, it is well known that the free energy of this reaction is very large and negative. The resulting value of Ke is $>>10^{10}$ for all temperatures. Therefore, the reaction tends strongly to go in the forward direction to completion. Although liquid phase thermodynamic properties are not well known, experience with molten ZrO_2 (Zircon arc lamp) shows expected stability. This property of ceramics is of course quite typical.

The rate of reaction of zirconium with oxygen would be expected to be pressure dependent since one of the reactants is a gas and the product is a solid. However, the rate of reaction of zirconium with steam would not necessarily be expected to be pressure dependent since there is no change in volume in the system by the reaction. Experimental data (Ref. 2) have shown that there is no effect of pressure at 1500 psi at a temperature of 2000^OF on the kinetics of the reaction between Zircaloy and steam. However, at lesser temperatures a pressure enhancement of up to a factor of 3 has been reported (Ref. 3 & 4). Thermodynamically, a mixture of hydrogen and oxygen will react spontaneously to form water at room temperature. Kinetically, it never happens in the absence of an ignition source.

Since the oxide formed on Zircaloy is protective and remains solid until dissolved by molten Zircaloy, the concept of a flame temperature for the reaction of massive Zircaloy (not a fine powder) with steam is not particularly meaningful. Experiments (Ref. 5-9) have demonstrated that massive zirconium and Zircaloy do not ignite in steam and do so in high pressure pure oxygen only if there is no oxide film present on the surface of the metal, regardless of the temperature of the metal. Since the oxide is soluble in the molten metal, the molten metal can ignite in oxygen if the oxide can be kept from covering the surface. But even molten zirconium will not ignite in steam, as the heat of reaction is not high enough to overcome the heat losses to the surroundings.

The paper of A. V. Grosse (enclosed with your letter), concerning the combustion of metals, describes the use of fine zirconium powder, not massive zirconium, in an oxygen jet to produce a high temperature flame. For very fine powder particles, the ratio of surface area to volume is sufficiently high that only a little reaction is required to melt the particle. Any finely powdered metal will produce a "flame" in an oxygen jet if it can form an oxide at such a temperature. Only those that do not produce a protective reaction product film can "ignite" in an oxidizing atmosphere in the massive form where conduction of heat away from the reacting surface can prevent its temperature rise.

There are two other very important factors that need to be considered in the determiniation of maximum temperature associated with the cladding-steam
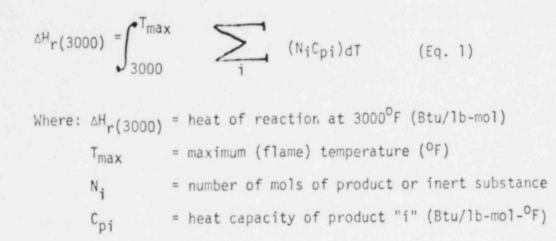
reaction. These are the thermal proximity of the UO_2 and Zircaloy and the contribution of the decay heat source. These factors are examined below with the aid of the attached Figure 1. The upper cladding temperature curve is identical to the calculation shown in SECY-80-107. The lower curve is the same calculation but without any zirconium-steam reaction. In the first calculation the reaction was complete at 406 seconds and the maximum cladding temperature was 6490°F. At 406 seconds in the second case the cladding temperature was 3000°F. Since both cases started at the same temperature (223°F) and had the same decay heat, the temperature contribution from decay heat in both cases was 2767°F. The reaction heat contribution to the maximum temperature was 3490°F (see Figure 1).

Within 10 seconds after completion of the reaction in Case 1, the cladding temperature drops to virtual thermal equilibrium with the fuel. From this time onward the cladding and fuel temperature were within 10°F of each other.

Several "flame" temperature calculations were performed to compare with the computer code calculations in Figure 1. The results are summarized in the attached Table 1.

The standard state for the reaction was considered to be at one atmosphere and 3000°F. The "products" listed in the table refer to reaction products (ZrO_2 and H_2) and inerts (UO_2) whose enthalphy change was considered in the flame temperature calculation. The higher value of reaction heat (256400 Btu/lb-mol) is equivalent to the single value used in our computer code TØØDEE2. The value of 210160 Btu/lb-mol value is from Brassfield's (Ref. 1) equation at 3000°F. The flame temperature formula used was:

$$\Delta H_{r(3000)} = \int_{3000}^{T_{max}} \sum_i (N_i C_{pi}) dT \qquad (Eq. 1)$$

Where: $\Delta H_{r(3000)}$ = heat of reaction at $3000^\circ F$ (Btu/lb-mol)

T_{max} = maximum (flame) temperature ($^\circ F$)

N_i = number of mols of product or inert substance

C_{pi} = heat capacity of product "i" (Btu/lb-mol-$^\circ F$)

Heats of dissociation were ignored since the reaction goes to virtual completion. The maximum temperature difference (ΔT_{max}) is $T_{max} - 3000^\circ F$ and is given to show the reaction heat contribution. The error in ΔT_{max} may be on the order of 20% because of the uncertainty in high temperature thermodynamic properties.

Cases 1 and 2 are tabulations of the TØØDEE2 results shown in Figure 1. Case 1, of course, is the actual cladding temperature, whereas Case 2 is the average of the fuel and cladding temperatures. This would be the condition if fuel and cladding were in thermal equilibrium. The degree to which Case 1 departs from equilibrium will be explained shortly.

Case 3 is a flame temperature calculation using Equation 1. The UO_2 was considered to be in thermal equilibrium with the cladding and was included in the right-hand side of Equation 1. In principle and in fact, Cases 2 and 3 are nearly equal. Case 3 then provides a check on the intended thermodynamics of the computer calculation.

Case 4 and flame temperature calculations through Case 7 used the lower value of reaction heat from Reference 1. Comparison of Cases 3 and 4 shows that by using a temperature dependent reaction heat the maximum temperature is reduced more than 300°F. This is because the heat of reaction becomes less at higher temperatures.

Case 5 can best be described as a "pure" flame temperature. Only the reaction products were considered. The temperature reached was the ZrO_2 boiling point (~7800°F).

Case 6 considers the UO_2 and the hydrogen. As expected, this produces the lowest temperature. This temperature difference (1950°F) is the maximum metal-water reaction effect that could be expected if, within a few seconds after complete reaction, good thermal contact exists between fuel and cladding.

Case 7 considers only ZrO_2 in the enthalphy balance. This case may be compared to Cases 2 and 3 to illustrate the effect of considering UO_2 in the balance. The UO_2 and ZrO_2 boiling points were taken to be 7800°F which was the temperature reached. Even Case 1 in which the UO_2 and cladding are coupled only by heat transfer is much closer to Cases 2 and 3 than Case 7.

Case 8 is presented for completeness per your request. This is the result for the zirconium-oxygen reaction. The oxide boiling point is also reached for this case.

In summary, the calculation of SECY-80-107 did consider thermodynamics. The limitations were clearly stated therein. Flame temperature analysis does not provide sufficient information about the relevant processes; specifically,

flame temperature analysis ignores the nature of massive zirconium reaction including kinetic effects. The calculations presented herein have shown that heat transfer and the presence of other substances (e.g., UO_2) are very important in determining maximum cladding temperatures.

Table 1

Maximum Zirconium-Steam Reaction With
Reactants Temperature at 3000°F Standard State

Case	Calculation	Products	ΔH_r (Btu/lb-mol)	T_{max} (°F)	ΔT_{max} (°F)
1	TØØDEE2	ZrO_2, UO_2	256400	6490	3490
2	TØØDEE2	ZrO_2, UO_2	256400	5330	2330
3	Equation 1	ZrO_2, UO_2	256400	5404	2404
4	Equation 1	ZrO_2, UO_2	210160	5075	2075
5	Equation 1	ZrO_2, H_2	210160	~7800	~4800
6	Equation 1	ZrO_2, UO_2, H_2	210160	4950	1950
7	Equation 1	ZrO_2 from H_2O	210160	~7800	~4800
8	Equation 1	ZrO_2 from O_2	473800	~7800	~4800

References

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FIGURE 1 ADIABATIC HEATUP FROM 48 SECONDS

CASE 1 With Zirconium-Steam Reaction

CASE 2 Without Zirconium-Steam Reaction

TIME - SECONDS

TEMPERATURE - DEGREES F