From: Sudhamay Basu, RES
To: JLS4 J. Staudenmeier, NRR
Date: Wed, May 3, 2000 10:27 AM
Subject: Fwd: spent pool accident

Joe,
As I said the attached information from Hee Chung is a draft. I will review it before it gets finalized. One thing you may want to note is that Hee is saying there is a scarcity of data on air oxidation of zircaloy. I have come across some very recent work in Europe on air oxidation. I am reviewing the work and at the same time, asking Hee to dig into it little more. So expect to see some significant modification of information on this topic. That's why I would consider the attached information very preliminary, strictly for your consumption.
Sud

R/19

From: Hee Mok Chung <heechung@anl.gov>
To: Sudhamay Basu <SXB2@nrc.gov>
Date: Mon, May 1, 2000 11:28 PM
Subject: spent pool accident

Sud, please find attached a draft writing on the subject (Word 5.1 format). I guess the next process is to: reflect your comments on the draft, run through a quick editing, and prepare a final copy in the form of a letter from me to you??! Hee

Spent Fuel Behavior Following Loss-of-Water Accident During Pool Storage

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1. Introduction

After discharge from a reactor, used fuel assemblies from light water reactors (LWRs) are stored and cooled in water in a spent-fuel pool. Under postulated accident situations during the storage, such as inadvertent drainage of the water and seismic events, spent fuel rods are expected to heat up following a loss of the water in the pool. The objective of this memo is to analyze and evaluate the sequence of metallurgical processes that are expected to occur in a fuel rod during the early stage of such an accident. More specifically, the memo addresses the issues of potential autoignition of Zircaloy cladding and potential release of fission products.

2. High-Burnup PWR Fuel Rod As a Bounding Case

The initial state of a LWR fuel rod at the onset of a postulated loss-of-water accident in a spent-fuel pool is influenced by many factors, such as reactor type (BWR or PWR), fuel burnup, reactor coolant temperature during operation, irradiation history, cladding material type (e.g., standard Zircaloy-4, low-Sn Zircaloy-4, liner Zircaloy-2, Zirlo, Zr-1Nb M5 alloy), fabrication variables, and length of storage in the pool.

In general, a high-burnup (burnup higher than ≈55 MWd/kgU) PWR fuel cladding fabricated from standard Zircaloy-4 exhibits more pronounced degradation than other types of fuel cladding. Therefore, for the purpose of the present evaluation, the behavior of this type of fuel rods will be analyzed as a bounding case.

3. Initial State of High-Burnup PWR Fuel Rod

High-burnup PWR fuel rods are characterized by several important microstructural features. These features, summarized in the following, play important roles in influencing the behavior of the fuel rod during a loss-of-water accident:

(1) Rim zone of the fuel pellet is consisted of Pu-rich powdery fuel particles or granules.

(2) The inner diameter (ID) of the cladding and fuel are bonded tightly through interdiffusion of Zr and U which forms a layer of monoclinic (Zr,U)O2.

(3) The thickness of the oxide layer at the cladding outer diameter (OD) could be ≈20 mm to ≈100 mm. The thickness is strongly dependent on grid span position.

(4) As a result of breakaway oxidation during in-reactor service, the OD-side oxide is porous and contains many interconnected microcracks. Within this breakaway oxide layer, steam or air

molecules could penetrate and migrate through the interconnected pores and microcracks more or less freely.

(5) In spite of the presence of thick breakaway oxide, the innermost layer of the OD-side oxide (which is in contact with the hydride-rich metal rim) is free of cracks or interconnected pores. Therefore, free gaseous penetration of steam is not possible through the innermost layer, and therefore, steam or air molecules cannot make a direct contact with the hydride-rich metal. The thickness of the innermost layer, containing high volume fraction of tetragonal ZrO2 of relatively high fracture toughness, ranges from ≈2 to ≈20 mm.

(6) The metal in contact with OD-side oxide contains d-phase Zr hydrides in high volume fraction (as high as ≈70 %). Hydride volume fraction in the midwall and the ID-side metal is low. These hydrides are aligned predominantly in the circumferential direction of the cladding.

(7) Significant level of residual stresses may be present in the oxide and metal which are produced in association with oxidation, rod bowing, and pellet-cladding mechanical interaction (PCMI).

4. Reaction of Zircaloy Cladding in Air

After the onset of a loss-of-water accident, water is assumed to be fully drained in a short period of time. The fuel cladding will be then exposed initially to steam-water mixture, steam, then steam-air mixture, and eventually to air.

In air, reaction of fresh (i.e., nonirradiated oxide-free) Zr or Zircaloy cladding is known to be faster than reaction in steam for a given cladding temperature [1]. A mixture of Zr oxide and Zr nitride, or probably Zr oxynitride, is formed in air as reaction product. Corrosion layer of Zr formed in air is characterized by distinctive gold or yellowish color which is in contrast to black or greyish-black color of Zr oxide formed in steam or oxygen.

According to the review given in Ref. 1, the reaction rate (i.e., weight gain) in air is several times faster than that in steam at >1100°C. In an unpublished work [2], reaction of fresh Zircaloy-4 was investigated at 1000-1450°C in air and steam environments. The result shows that for 1100°C, the rate of oxide layer growth is ≈1.8 times faster in air than in steam. Although a sufficient data base is not available at this time that allows similar quantitative comparison of reaction rates in air and steam for <1000°C, it seems reasonable to assume that reaction rates (i.e., conversion of Zr to corrosion products Zr oxide or oxynitride) at the lower temperatures are faster in air than in steam.

Reaction at <600°C either in steam or in air in spent-fuel container is probably not much concern, simply because the rate is too slow, and there would be days or weeks of time available to be able to detect the occurrence of a loss-of-water accident and to implement a mitigating measure.

Breakaway oxidation of Zircaloy cladding in steam does not occur at high temperatures, e.g., at >700°C, except in hydrogen-rich steam-hydrogen mixture that is produced at the narrow pellet-cladding gap near a ballooned and burst cladding during a LOCA-like time-temperature excursion in steam [3]. However, breakaway oxidation was observed in air even at 1000-1450°C [2]. At <700°C, breakaway oxidation will

be more pronounced than at the higher temperatures. Therefore, it is fair to assume that a breakaway corrosion layer that contains interconnected microcracks and pores is formed on the OD surface of the cladding following a loss-of-water accident and subsequent heatup.

5. Crack-Free Adherent Innermost Oxide Layer

The stoichiometry and structure of the oxide layer, produced in steam or oxygen, vary as function of its location relative to phase boundaries, i.e., from the coolant-oxide boundary to the oxide-metal boundary. The oxide near the coolant-oxide boundary has a higher oxygen stoichiometry, monoclinic structure, and relatively lower fracture toughness. In contrast, the oxide near the oxide-metal boundary has a lower stoichiometry, higher volume fraction of tetragonal phase, and relatively higher fracture toughness. As a result, the OD-side metal (or metal-hydride composite in high-burnup fuel cladding) is always covered with an innermost oxide layer that is virtually a tetragonal phase and that is tightly adherent to the metal. Most of all, this innermost oxide layer is free of microcracks. Therefore, a direct contact of gaseous molecules of steam, oxygen, or hydrogen with the underlying metal is not possible; they can reach the metal only through permeation through the crack-free adherent innermost oxide layer. The thickness of such innermost oxide layer ranges from ≈2 mm to ≈20 mm, depending on cladding type, fabrication, fluence, fuel burnup, and irradiation history.

This feature, characteristic of Zircaloy oxidation, is an important factor that must be considered to evaluate the potential for autoignition during a loss-of-water accident. Similar crack-free innermost oxide or oxynitride layer is formed in air, at least at >1000°C. However, this feature needs to be verified for lower temperatures, preferably for oxide-covered spent-fuel cladding that is subsequently oxidized in air.

6. Exothermic Heat of Reaction of Zr and Zr Hydride

The exhothermic heats (per mole of Zr reacted) of reaction of Zr and Zr hydride in steam, oxygen, and steam environments are listed below:

$Zr + O_2 = ZrO_2 + 2H_2$	DHo = -1100.6 kJ (260 kcal)
$Zr + 2H_2O$ (steam) $= ZrO_2 + 2H_2$	DHo = -617 kJ (147 kcal)
$Zr + H_2 = ZrH_2$	DHo = -169 kJ (40.3 kcal)
$Zr + 1/2N_2 = ZrN$	DHo = -87.2 (20.8 kcal)
$ZrH_2 + O_2 = ZrO_2 + H_2$	DHo = -931.6 kJ (223 kcal)
$ZrH_2 + H_2O$ (steam) $= ZrO_2 + 3H_2$	DHo = -448 kJ (107 kcal)

This information indicates that, UNDER OTHERWISE IDENTICAL CONDITIONS, autoignition of Zr or Zr hydride in oxygen (and hence, in air) is more likely to occur than autoignition of Zr (or fresh clean Zircaloy

metal) in steam.

7. Potential for Autoignition

Autoignition can occur in Zr-base alloys and Zr hydride in association with the unusually large exothermic heats of oxidation and fast oxidation rate, which produce exceedingly high rate of heating than the rate of heat loss, thereby increasing the material temperature rapidly. As the temperature increases, the reaction rate increases further, driving a further acceleration of heat generation, leading to a classical autocatalytic reaction.

For autoignition to occur, three conditions must be met at the same time: (1) sufficiently high temperature of the material, (2) sufficiently high surface-to-volume ratio of the material, and (3) clean surface of material (Zircaloy or Zr hydride) in contact with the environment. A pile of fine freshly machined Zr turnings or powders that are exposed to moist air is one of the worst cases, and autoignition of such piles have been reported even at room temperature. However, the situation for spent fuel cladding under the conditions of loss-of-water accident situation is very much different.

7.1 Potential for Autoignition Before Cladding Burst

Zr hydrides in spent fuel cladding are present in the metallic Zircaloy as dispersed second-phase material. As pointed out previously, this metal-hydride composite is always covered with either Zr oxide, Zr nitride, or Zr oxynitride. Therefore, gaseous oxygen or air molecules cannot directly contact the metal-hydride composite. The potential for spontaneous cracking of this innermost oxide or oxynitride layer during exposure to air at <700°C is extremely unlikely. Therefore, unless some type of impact force is applied to the fuel rod accidentally or intentionally, potential for autoignition, before occurrence of cladding ballooning and burst (i.e., at temperatures lower than ≈700°C), is extremely unlikely.

7.2 Potential for Autoignition at the Moment of Cladding Burst

By the time the cladding temperature reaches >750°C, most Zr hydrides are dissolved in the metal, because the solubility of hydrogen in Zircaloy metal increases significantly with increasing temperature. Hydride dissolution will be more pronounced when the heatup rate is relatively slow, e.g., the rates reported by Benjamin et al. [4]. At the same time, most irradiation-induced damages and hardening centers are annealed out.

As a consequence, mechanical strength of the cladding decreases significantly, even for high-burnup fuel. Therefore, by the time cladding temperature reaches higher than approximately 750°C, ballooning and burst of the cladding will occur inevitably. For >750°C, it is reasonable to assume that burst occurred in most fuel cladding. The higher the fuel burnup, the lower the burst temperature. This is because the internal pressure of a rod increases with burnup.

At the moment of burst, clean (i.e., oxide-free) and hot (e.g., ≈750-850°C) Zircaloy metal (or metal-hydride composite) will be abruptly exposed to air. Potential for autoignition at this moment needs to be evaluated carefully. Although the surface state of the metal or metal-hydride composite is clean and the material temperature is high, the surface-to-volume ratio of the air-exposed material is low, because only the circumferential cross section of the cladding metal is exposed and the rest of the metal remains covered with oxide or oxynitride.

For similar burst conditions that occurred during simulated LOCA-like heatup tests, it has been well established that autoignition of Zircaloy cladding did not occur in steam. In many LOCA tests conducted in many laboratories on nonirradiated Zircaloy cladding in steam, no autoignition has been reported. For example, no autoignition was observed during burst tests of nonirradiated cladding tubes in stagnant steam at ≈650-1300°C [5]. In the study, ballooning and burst sequences were recorded on high-speed color videotapes. The video record shows that only a localized hot spot is developed at the burst location, followed by prompt disappearance of the hot spot within several seconds without an ignition.

For high-burnup PWR fuel, burst are expected to occur in air at ≈750-850°C during a postulated loss-of-water accident during pool storage. Therefore, it is necessary to take account of the effects of the higher oxidation rates in air (e.g., a factor of ≈2) and the significantly larger heat of oxidation (i.e., ≈1100 kJ per mole of Zr in air vs. ≈617 J in steam). Considering the combined effect of the two factors, a burst in air at ≈800°C can be assumed to be equivalent to a burst in steam at ≈1100°C. Because autoignition of a burst spot was not observed to occur in steam at least up to ≈1300°C, this means that autoignition in air at ≈800°C is unlikely to occur.

However, it may be necessary to confirm the result of this analysis through actual burst tests in air.

7.3 Potential for Autoignition After Cladding Burst

After burst, the ID-side surface of the burst cladding will be exposed continuously to air-fission-gas mixture and then air at >750°C. By this time, steam is absent in the environment; therefore, generation of hydrogen gas from oxidation of the ID surface of the burst cladding is negligible. Therefore, potential for ignition of air-steam-hydrogen or air-fission-gas-hydrogen mixture is not a concern. Furthermore, tight cladding-pellet bonding is formed after operation to burnups higher than ≈55 MWd/kgU, and the bonded layer is not likely to be separated during burst. Therefore, the ID surface of a burst cladding will remain covered with a layer of (Zr,U)O2.

8. Fission Gas Release After Cladding Burst

Once cladding ballooning and burst occur, fission gas will be released freely to the pool containment. To prevent cladding burst and fission gas release, cladding temperature must be limited conservatively to no higher than ≈700°C. If maximum cladding temperature could be limited to <700°C, potential for

autoignition as well as fission gas release would be of little concern.

References

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[2] H. M. Chung, unpublished work, Argonne National Laboratory, 1980.

[3] H. M. Chung and T. F. Kassner, "Embrittlement Criteria for Zircaloy Fuel Cladding Applicable to Accident Situations in Light□Water Reactors: Summary Report," NUREG/CR-1344, ANL-79□48 (January 1980).

[4] A. S. Benjamin, D. J. McCloskey, D. A. Powers, and S. A. Dupree, "Spent Fuel Heatup Following Loss of Water During Storage," NUREG/CR-0649, SAND77-1371, Sandia Laboratories, March 1979.

[5] H. M. Chung and T. F. Kassner, "Deformation Characteristics of Zircaloy Cladding in Vacuum and Steam Under Transient-Heating Conditions: Summary Report," NUREG/CR-0344, ANL-77-31, July 1978.

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