

FOIA

**From:** Hee Chung <heechung@anl.gov>  
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**Date:** Fri, Oct 13, 2000 5:20 PM  
**Subject:** Refs. for Hydride in SFPool

Sud, I have compiled below a list of references that should be helpful to address hydride behavior during a spent-fuel-pool loss-of-water accident (LOWA) situation. A short summary of each Ref. is also given. We can discuss details early next week.

As I understand it, the first specific point was: (1) are there sufficient evidences that Zr hydrides, rich in many spent fuel cladding, dissolve back into the metal as the cladding reaches about 700 °C, at which time cladding is expected to burst and fresh oxide-free surface of metal+hydride composite could be abruptly exposed to air? The way I see it, if the answer is yes, it could impact the potential for autoignition and, or, exacerbate the onset of runaway oxidation near the burst region. However, the answer appears to be no. The second point was: (2) will hydrides lead to oxide spallation (exfoliation, not my favorite term) during sfp LOWA heatup? This is also unlikely. Let us consider using the following Refs.:

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1. R. L. Beck, Trans. ASM 55 (1962) 542

This paper gives unirradiated Zr-H binary phase diagram. It shows that H solubility in hcp alpha Zr increases from about 60 wppm at 300C to about 700 wppm at 600C. At about 560-590C, some alpha Zr transforms to bcc beta Zr, forming alpha+beta two phase. H solubility in beta Zr is very very high, about 9000 (nine thousand) wppm at about 700C. Therefore, most H atoms at >590C will diffuse from alpha to beta Zr in unirradiated unalloyed Zr. However, Zircaloy-2 and -4 have significantly higher alpha-to-beta transformation temperature than Zr.

2. H. M. Chung and T. F. Kassner, J. Nucl. Mater. 84 (1979) 327.

→ This paper shows that alpha-to-beta transformation starts at 815C in unirradiated Zircaloys that contain <25 wppm H. Oxygen is an alpha stabilizer and H is a beta stabilizer, and most spent-fuel cladding (sfc) contains 0.1-0.2 wt.% O and 100-300 wppm H. Some high-burnup PWR sfc (fabricated from standard Zircaloy) contains H as much as 500-900 wppm. Therefore, alpha-to-beta transformation in sfc is expected to start at about 800C (at the slow heating rate expected under sfp LOWA situation). H diffusivity in alpha Zircaloy at >800C is very high. Therefore, hydrides in Zircaloy cladding, unstable at >800C, dissolves fast in alpha Zircaloy, and virtually all H solute atoms diffuse to beta Zircaloy rapidly. At >800C, hydrides are not an issue.

3. J. J. Kearns, J. Nucl. Mater. 22 (1967) 292.

This paper shows that H solubility in unirradiated Zircaloy-2 and -4 increases from about 90 wppm at about 300C to about 900 wppm at about 600C, a behavior similar to that of unirradiated Zr.

4. A. McMinn, E. C. Darby, and J. S. Schofield, "The Terminal Solubility of Hydrogen in Zirconium Alloys." Proc. of Zirconium in the Nuclear Industry: 12th International Symposium, June 15-18, 1998, Toronto, Canada. This paper shows that H solubility at about 320C in irradiated PWR sfc is somewhat higher than that of unirradiated Zircaloys, i.e., 150-300 vs. 100 wppm. Therefore, majority of H atoms in medium- and high-burnup sfc in pool at about 80-90C will be present as hydrides.

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However, as sfc heats up to about 600-700C, H solubility will increase to at least 900 wppm. Therefore, hydrides in sfc will be thermodynamically unstable by the time sfc reaches about 600-700C and dissolve into alpha Zircaloy under the slow heatup condition of an sfp LOWA. No direct evidences for this are not available in literature. However, the following Refs. report evidences of hydride dissolution in sfc under somewhat different (isothermal) conditions.

5. R. E. Einziger and R. Kohli "Low-Temperature Rupture Behavior of Zircaloy-Clad Pressurized Water Reactor Spent Fuel Rods Under Dry Storage Conditions." Nucl. Technology, 67 (1984) 107.  
In this work, medium-burnp (32 MWd/kgU) PWR sfc was heated to 332C for up to 2100 h under 140 MPa-applied-hoop stress and slowly cooled. Significant reorientation (i.e., formation of radial hydride) of circumferential hydrides (present in as-spent condition) was evident. For hydride reorientation to occur, three conditions should be met: (a) dissolution of the circumferential hydrides, (b) sufficiently high hoop stress, and (c) slow cooling rate. Therefore, this work shows that significant hydride dissolution occurred at 332C in the PWR sfc.

6. W. Goll, H. Spiker, and E. Toscano, "Short-Time Creep and Rupture Tests on High Burnup Fuel Rod Cladding," J. Nucl. Mater. in press.  
Similar to the experiment of Ref. 5, PWR sfc (burnup 64 MWd/kgU) was pressurized, heated to and held at 300-370C, and slowly cooled down. Extensive hydride reorientation was evident, showing that significant dissolution of circumferential hydrides occurred.

7. CEA LEC Note Technique No. 94/2015 Ind: A, "Examens Destructifs sur le Crayon FABRICE Issu du Crayon 5 Cycles GRAV2-Q02, apres tir "REP Na-1" dans CABRI, Part I: Recherche d'un Effect Systeme," by P. Menut, 1994.  
This report shows many metallographs of a PWR sfc section (standard Zircaloy-4, Graveline PWR, 5 cycle, load-following operation) that was exposed without an applied stress to about 380C for about 13 h and then pulse-loaded at 280C under an RIA-like condition. Extensive redistribution of the originally circumferential hydrides, present in as-spent condition, is evident, indicating that virtually all the circumferential hydrides dissolved at 380C.

Refs. 5-7 provide direct evidences that hydrides in medium- and high-burnup sfc dissolve readily by holding at 330-380C for hours. If sfcs were heated to 700C, the process will be greatly accelerated. Under sfp LOWA conditions, most calculations indicate that 700C will be reached in about 1-1.5 h. At this low heatup rates, it is expected that virtually all hydrides will be dissolved in the alpha Zircaloy by the time the temperature reaches about 700C.

Therefore, abrupt exposure of hot Zr hydrides to air at the moment of cladding burst is considered very unlikely to occur. However, abrupt exposure of clean metal will be inevitable, which will be followed by locally accelerated two-sided oxidation of the cladding near the burst opening. Whether instantaneous autoignition of the clean metal cross section (at the moment of burst) is possible, or is entirely out of question, I really don't know. If autoignition occurs, sustained propagation of the burning front is considered to be unlikely.

On the second point of oxide spallation, I have the following opinion on three types of oxides spallation:

A. The fracture toughness of Zr oxide is strongly influenced by temperature, as well as the crystal structure, monoclinic, tetragonal, or mixture. Oxide in sfc in as-spent condition is mostly monoclinic, with increasing amount of retained tetragonal phase near the metal.

B. Load-following operation produces large cyclic loading. Most evidences of oxide spallation were reported for load-followed PWR high-burnup fuel fabricated from standard Zircaloy-4, e.g., the Graveline PWR fuel in Ref. 6 (i.e., the famous or infamous REP Na-1 test). Without load-following operation in US, oxide spallation during operation is unlikely or insignificant. Some limited report of oxide spallation in US fuels based on visual inspection of surface oxide morphology is not a sufficient evidence; it must be verified by destructive metallography.

C. Therefore, oxide spallation and associate presence of large hydride blisters are likely to be insignificant in most US sfc stored in pools.

D. However, limited oxide spallation during transport is possible. Spalled oxide observed without a matching hydride blister indicates that the spallation occurred during transportation and/or during the mounting procedure in hot cell.

E. During heatup in an sfp LOWA, oxide spallation is not likely to occur because the higher the temperature, the higher the toughness of oxide. Zr oxide at about  $>800^{\circ}\text{C}$  is in fact ductile. This is also likely to be true even for high-burnup sfcs in which dense hydrides are present in as-spent condition. As they are heated up, hydrides will start to dissolve and the toughness of oxide will increase, a condition not conducive for oxide spallation.

Please call Monday or Tuesday.  
Hee

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