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DEVELOPMENT REPORT

INTERNAL HYDRIDING IN IRRADIATED DEFECTED ZIRCALOY FUEL RODS—A REVIEW

(LWBR Development Program)

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J. C. Clayton

October 1987

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BETTIS ATOMIC POWER LABORATORY

WEST MIFFLIN, PENNSYLVANIA 15122-0079

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FOREWORD

The Shippingport Atomic Power Station located in Shippingport, Pennsylvania was the first large-scale, central-station nuclear power plant in the United States and the first plant of such size in the world operated solely to produce electric power. This program was started in 1953 to confirm the practical application of nuclear power for large-scale electric power generation. It has provided much of the technology being used for design and operation of the commercial, central-station nuclear power plants now in use.

Subsequent to development and successful operation of the Pressurized Water Reactor in the Atomic Energy Commission (now Department of Energy, DOE) owned reactor plant at the Shippingport Atomic Power Station, the Atomic Energy Commission in 1965 undertook a research and development program to design and build a Light Water Breeder Reactor core for operation in the Shippingport Station.

The objective of the Light Water Breeder Reactor (LWBR) program has been to develop a technology that would significantly improve the utilization of the nation's nuclear fuel resources employing the well-established water reactor technology. To achieve this objective, work has been directed toward analysis, design, component tests, and fabrication of a water-cooled, thorium oxide-uranium oxide fuel cycle breeder reactor for installation and operation at the Shippingport Station. The LWBR core started operation in the Shippingport Station in the Fall of 1977 and finished routine power operation on October 1, 1982. After end-of-life core testing, the core was removed and the spent fuel shipped to the Naval Reactors Expended Core Facility for detailed examination to verify core performance including an evaluation of breeding characteristics.

In 1976, with fabrication of the Shippingport LWBR core nearing completion, the Energy Research and Development Administration, now DOE, established the Advanced Water Breeder Applications (AWBA) program to develop and disseminate technical information which would assist U.S. industry in evaluating the LWBR concept for commercial-scale applications. The AWBA program, which was concluded in September, 1982, explored some of the problems that would have been faced by industry in adopting technology confirmed in the LWBR program. Information developed includes concepts for commercial-scale prebreeder cores which would produce uranium-233 for light water breeder cores while producing electric power, improvements for breeder cores based on the technology developed to fabricate and operate the Shippingport LWBR core, and other information and technology to aid in evaluating commercial-scale application of the LWBR concept.

All three development programs (Pressurized Water Reactor, Light Water Breeder Reactor, and Advanced Water Breeder Applications) have been conducted under the technical direction of the Office of the Deputy Assistant Secretary for Naval Reactors of DOE.

Technical information developed under the Shippingport, LWBR, and AWBA programs has been and will continue to be published in technical memoranda, one of which is this present report.

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LIST OF ABBREVIATIONS AND ACRONYMS

AWBA	Advanced Water Breeder Applications
CHORT	Corrosion and Hydriding of Reactor Tubing (a computer program)
DOE	Department of Energy
EFPH	Effective Full Power Hours
GRIP	Grid Rod In-Pile (a LWBR irradiation test)
LWBR	Light Water Breeder Reactor
PCI	Pellet-Cladding Interaction
PWR	Pressurized Water Reactor

Although not a problem in recent commercial power reactors, including the Shippingport Light Water Breeder Reactor, internal hydriding of Zircaloy cladding was a persistent cause of gross cladding failures during the 1960s. It occurred in the fuel rods of water-cooled nuclear power reactors that had a small cladding defect. This report summarizes the experimental findings, causes, mechanisms, and methods of minimizing internal hydriding in defected Zircaloy-clad fuel rods. Irradiation test data on the different types of defected fuel rods, intentionally fabricated defected and in-pile operationally defected rods, are compared. Significant factors affecting internal hydriding in defected Zircaloy-clad fuel rods (defect hole size, internal and external sources of hydrogen, Zircaloy cladding surface properties, nickel alloy contamination of Zircaloy, the effect of heat flux and fluence) are discussed. Pertinent in-pile and out-of-pile test results from Bettis and other laboratories are used as a data base in constructing a qualitative model which explains hydrogen generation and distribution in Zircaloy cladding of defected water-cooled reactor fuel rods. Techniques for minimizing internal-hydride failures in Zircaloy-clad fuel rods are evaluated.

INTERNAL HYDRIDING IN IRRADIATED DEFECTED ZIRCALOY FUEL RODS - A REVIEW

(LWBR Development Program)

J. C. Clayton

SECTION 1 - INTRODUCTION

The hydriding characteristics of Zircaloy tubing are of interest to reactor designers because of the widespread use of Zircaloy cladding for oxide-pelleted fuel rods in water-cooled nuclear power reactors. Internal hydriding of the Zircaloy cladding was a persistent cause of defects and occasional failures in early commercial fuel rods (References 1 and 2).

The purpose of this review, conducted as part of the Shippingport Light Water Reactor Breeder Reactor (LWBR) Development Program, is to summarize the test data, causes, mechanisms, and methods of minimizing internal hydriding failures in defected Zircaloy-clad fuel rods.

SECTION 2 - PROBLEM HISTORY AND DESCRIPTION

2.1 - DEFECTED VERSUS FAILED FUEL RODS

A defect is defined as a breach of cladding integrity, i.e., a perforation (slit, crack, or pinhole) that leaks fission products to the coolant and coolant to the rod internals. Many defected Zircaloy-clad fuel rods operated satisfactorily without diminishing core performance (Reference 1). A fuel rod failure is defined as loss of cladding integrity, high coolant activity level, and contamination of the coolant by particulate fuel.

2.2 - TYPES OF ZIRCALOY FUEL ROD HYDRIDING

Two types of hydriding, external hydriding produced by hydrogen outside the fuel rod and internal hydriding due to causes inside the fuel rod, were identified in Zircaloy-clad fuel rods (References 1 through 5). Internal hydriding is further classified as primary or secondary hydriding. Primary hydriding is generated internally in an initially undefected Zircaloy fuel rod. Its sources are hydrogenous contaminants (moisture, oil, grease, etc.) introduced into the fuel rod during fabrication as well as any residual hydrogen in the oxide fuel resulting from the hydrogen sintering operation (Reference 6). In secondary hydriding, the initial breach of the Zircaloy cladding is caused either by primary hydriding itself or by a nonhydride related incident which allows coolant to enter and hydride the rod. Examples of a nonhydriding incident include stress-corrosion cracking induced by pellet-cladding interaction, power ramp, aggressive fission product attack, rod-to-rod contact causing high cladding temperatures, cladding wear at support grid contact points, etc. This report addresses the problem of secondary hydriding, mainly in pressurized water reactors (PWRs) where the coolant contains some dissolved hydrogen.

2.3 - AMOUNTS OF HYDROGEN PICKUP IN ZIRCALOY

Hydrogen pickup in Zircaloy fuel rods falls into three categories: expected due to corrosion, accelerated, and massive (Reference 7). Expected hydrogen pickup results from the additional hydrogen which enters the Zircaloy

cladding through the ZrO_2 corrosion film (approximately 50-500 ppm). Accelerated hydriding is defined as hydrogen absorption from the coolant far in excess of the nominal 25 percent pickup fraction of free H_2 produced by the $Zr-H_2O$ corrosion reaction for Zircaloy-4 (approximately several thousand ppm). Massive hydriding is the formation of regions of delta phase zirconium hydride in the cladding due to grossly accelerated hydrogen pickup (16,300 ppm). At operating temperatures for PWRs, zirconium is thermodynamically unstable with respect to hydrogen and should completely hydride. The protective corrosion oxide surface film prevents the gaseous hydrogen in the coolant from reacting with the bare Zircaloy.

SECTION 3 - IN-PILE DEFECTED FUEL ROD TEST DATA

3.1 - BETTIS LABORATORY TESTS

3.1.1 - Pre-LWBR Tests

The Bettis Laboratory was one of the first to study the behavior of defected Zircaloy-clad UO_2 fuel rods in-pile and the factors affecting the limit of their performance (References 1, 8, and 9). The initial work was carried out in the 1950s in support of the Shippingport PWR Core I blanket rods. Excessive cladding hydriding was observed in both intentionally defected rods and in rods that operationally defected in-pile (unintentionally defected). Hydrogen contents of 100-200 ppm were found in cladding near defects and 1400 ppm at the ends of the rods (Reference 8). It was concluded either that the intentionally fabricated defect holes of some rods became plugged or that areas of the rod away from the defect hole became effectively isolated and behaved as though the rods were not defected. In any case, the cladding of these rods became stressed and ruptured during irradiation with resultant hydriding.

Since 1960, massive internal hydriding was found only in rods that operationally defected in-pile (References 10 through 15). Sixteen such in-pile defected rods were observed. Fuel compositions were mainly UO_2 , ZrO_2-UO_2 , and UO_2-ZrO_2-CaO . Irradiation periods in the defected state after cladding rupture varied from about five minutes to approximately 200 days. Cladding cracking, both ductile and brittle, was attributed to bad welds, burnout caused by molten fuel, cladding instability due to fuel swelling, and waterlogging*. All 16 rods were destructively examined, and extensive areas of massive internal hydride were detected in 13 of them. Both accelerated and massive hydriding occurred at remote locations from the defect. Two of the remaining rods were found to have brittle cladding fractures. Hydride was observed mainly in the cladding near the end caps. The cladding over the fuel stacks was

* Waterlogging is deformation of the cladding caused by excessive internal fuel rod pressure of entrapped coolant as it flashes to steam during a power increase.

relatively free of hydride. The last rod waterlogged and displayed only an overall high hydrogen content in the cladding (about 300 ppm) but did not exhibit massive hydriding.

Thirty intentionally fabricated defected rods were also tested during this period (1960-1970). These rods were fabricated with various pellet geometries (annular, dished-end, solid), pellet densities (84-98 percent theoretical), and fuel materials (UO_2 , $\text{ZrO}_2\text{-UO}_2$, $\text{ThO}_2\text{-UO}_2$). The irradiation performance of these intentionally defected rods was satisfactory. Postirradiated fuel structures ranged from that of the preirradiated structures to almost total fuel melting.

Three cases of waterlogging occurred in these intentionally fabricated defected rods. Cladding diameter swelling was measured in a UO_2 -fuel and a $\text{ZrO}_2\text{-UO}_2$ -fuel rod. Another $\text{ZrO}_2\text{-UO}_2$ -fuel rod ruptured resulting in cladding hydrogen concentrations of about 500 ppm, but massive internal hydriding was not found (Reference 16). This failure was attributed to excessive plastic straining caused by repeated waterlogging incidents during irradiation. With the exception of the ruptured rod, there were no detectable fuel losses associated with the irradiation of these 30 intentionally defected fuel rods.

Six of these intentionally defected rods contained $\text{ThO}_2\text{-UO}_2$ fuel. There were no unusual incidents during the irradiation of these rods indicating satisfactory performance.

The pre-LWBR test data can be summarized as follows:

- a. Fuel rods with intentionally fabricated defects generally did not excessively hydride.
- b. Fuel rods which defected in-pile generally had areas of accelerated or massive hydriding.

3.1.2 - LWBR Tests

The Shippingport LWBR core contained 12 hexagonal-shaped modules which were arranged in a symmetric array surrounded by 15 reflector modules (Reference 17). Each of the hexagonal fuel modules contained a central movable seed assembly surrounded by a stationary blanket assembly. The fuel was ThO_2 and

ThO₂-UO₂ pellets which were sealed in Zircaloy-4 tubes. The absence of higher-than-expected coolant activity during operation indicated that there was no detectable breach of the cladding in any of the LWBR rods.

As part of the LWBR irradiation test program, 19 fuel rods (14 seed and 5 blanket) were intentionally defected with drilled holes (0.005-inch diameter) prior to testing. In addition, two blanket test rods developed small cladding defects during planned in-service transient testing. The transient testing was at higher heating rates than occurred during LWBR reactor operations.

All 21 defected test rods operated successfully with limited radioactivity release to the coolant (Reference 7). No significant ThO₂ or ThO₂-UO₂ fuel erosion was detected (Reference 18). Due to the greater internal surface corrosion, the total hydrogen content in the defected rod cladding was several times those in nondefected rod cladding with similar irradiation histories (100-500 ppm compared to 30-70 ppm hydrogen). A pronounced variation in hydride concentration was observed through the cladding wall thickness of the defected rods. Hydrogen levels in the cladding were higher at the external surface than at the internal surface because hydrogen diffuses toward the cooler region in a sufficiently high thermal gradient (Figure 1). The hydride concentrations for nondefected rod cladding were relatively uniform.

Hydrides in the vicinity of the defect hole were generally low in concentration with typical uniform levels of about 100 ppm. This might occur from hydrogen escaping through the defect hole resulting in a low H₂/H₂O ratio or hydrogen diffusion to adjacent cooler cladding areas. Evidence of hydrogen migration to cooler regions of the rods remote from the defect hole was observed, indicating that local hydrogen levels are not always proportional to corrosion oxide thickness in defected rods.

Instances of localized accelerated and massive hydriding were detected in three intentionally defected and one operationally defected fuel rod (Figure 2). None of these incidents interfered with the operation of the irradiation tests. For example, one rod which defected in service due to iodine stress-corrosion cracking operated successfully for about 12,000 effective full power

Cladding Outer
Surface

Cladding Inner
Surface

(a) ~200 ppm Hydrogen (Average)

(b) ~1000 ppm Hydrogen (Average)

Figure 1. Hydrogen Gradients in GRIP IIIB Rod 79-609D (X250)

Figure 2. Accelerated and Massive Hydriding in GRIP IIIB Rod 79-609D (X100)

hours (EFPH)*. This rod was operational even though during postirradiation examination the cladding was observed to be massively hydrided near the bottom end of the rod (Reference 7). None of these hydrided rods lost structural integrity during operation, which attests to their ability to function under localized and massive hydriding conditions.

3.1.3 - AWBA Tests

The Advanced Water Breeder Applications (AWBA) program used a duplex pellet concept. The duplex pellet design consisted of a cylindrical thorium central core inside an oxide annulus which contained the initial fissile material. Transmutation of the thorium in the duplex pellet to uranium-233 provides fuel for use in subsequent breeders. The irradiation test program supporting development of the duplex fuel pellet included three intentionally fabricated defected rods, two with UO_2 and one with ThO_2 - UO_2 annuli (References 19 and 20).

Some slight erosion was noted in the UO_2 -fueled defected rod. The irradiation performance of the ThO_2 - UO_2 -fueled defected rod compared favorably with that of the LWBR solid ThO_2 - UO_2 pellet irradiation tests. Circumferential white corrosion rings were observed on the outside cladding surface of the defected rod with the ThO_2 - UO_2 annulus at the locations of 50-mil thick ThO_2 spacers separating the duplex pellets in the fuel stack. Neutron radiography and metallographic examination of the cladding showed that the white corrosion rings were associated with substantial nonuniform concentrations of hydrogen in the cladding, with the regions affected by the corrosion rings coinciding with the regions of heaviest hydrogen concentration. In regions of cladding adjacent to the ThO_2 - UO_2 annulus, hydrogen concentrations ranged from <100 ppm near the inner surface to several hundred ppm or more near the outer surface. In the cooler cladding adjacent to ThO_2 spacer pellets, much higher concentrations of hydrogen were observed. These concentrations varied from about 500 ppm near the inner surface to approximately 12,000 ppm in a rim about 3 to 5 mils thick at the outer surface. The fuel stack arrangement in

* EFPH are the hours of operation multiplied by the fraction of rated power.

this rod, consisting of pellets containing the fissile material (with high power and heat generation) interspersed with the ThO_2 spacers (with lower power and heat output), generated hydrogen cold traps in the cladding.

Diameter measurements revealed ridging of the cladding at the locations of the white corrosion rings. The average diametral ridge height was 0.8 mil with a maximum of 1.2 mils. This ridging could be caused by the volumetric increases associated with the extensive hydriding. Subsequent development of the accelerated white corrosion rings then resulted from disturbances in the protective corrosion film due to local straining and/or reduced corrosion resistance of zirconium hydride.

3.2 - NON-BETTIS DEFECTED ROD TESTS

Hydriding data from irradiation tests of defected rods conducted by other organizations but pertinent to the Bettis irradiation test programs are summarized below.

3.2.1 - Location of Hydriding in Fuel Rods

Examination of UO_2 - PuO_2 -fueled intentionally defected test rods showed little hydriding in the immediate vicinity of the defect hole (Reference 21). Both accelerated and massive hydriding were observed in UO_2 - and UO_2 - PuO_2 -fueled rods at locations remote from the defect opening, often in lower power regions, where protective corrosion oxide films were thinnest (References 8, 21 through 25). For example, hydrogen contents of 100 to 200 ppm (normal corrosion hydriding) were found near the rupture area and 1400 ppm (accelerated hydriding) at the end of Zircaloy-clad UO_2 fuel rods that failed after operating for 200 days at heat fluxes of approximately 400,000 BTU/hr/ft^2 (Reference 8). In most defected rod tests, there were no indications of massive hydriding in the cladding of intentionally defected rods; but accelerated hydriding was often found at remote locations from the defect.

3.2.2 - Inside Surface Corrosion Oxide Film Properties

During in-pile testing of defected fuel rods, coolant water enters the fuel-cladding gap via the defect opening and becomes steam at operating temperatures. This results in corrosion of the inner Zircaloy cladding surface

in addition to normal corrosion of the outer cladding surface. Corrosion oxide forms on both surfaces, but corrosion rates and corrosion oxide film thicknesses of the internal cladding surface are greater than those of the outer surface due to higher temperatures and radiation-enhanced effects at the inner surface. For the LWBR defected irradiation test rods (Section 3.1.2), the thickness of the inner surface oxide varied. It was greatest at and near the higher temperature peak power positions where the defect holes were drilled and thinnest in the low temperature, low power regions near the rod ends. Similar results were found in postirradiation examination of defected European Zircaloy fuel rods, i.e., a thicker inside oxide layer occurred near the defect (References 24 and 25). As illustrated in Figure 3, thickness of the inner surface oxide decreases with increasing distance from the defect opening.

Occasionally, local oxide patches with accelerated hydriding were observed opposite radial pellet cracks (References 24 and 25). It was postulated that these high hydrogen/oxide patches are the result of local attack on the normally protective oxide film by aggressive fission products such as cesium and iodine (References 8, 24, and 25). Defects in the cladding inside oxide film can arise due to strain concentrations opposite pellet cracks and interfaces combined with fission product attack. The effect of fission products, more of which are released at the higher heat ratings, could be to increase the onset of localized accelerated hydriding by destroying the protective qualities of the ZrO_2 corrosion film (References 8, 22, 24 through 26).

3.2.3 - Thermal Migration of Hydrogen in Zircaloy Cladding

Reports of metallographic detection of radial thermal diffusion of hydrogen from the hotter inside cladding surfaces to the cooler outside regions of defected Zircaloy rods are common (References 8, 21, and 25). As reported in Section 3.1.3, both radial and localized axial migration to colder cladding areas were observed in an intentionally defected AWBA rod resulting in substantial nonuniform concentrations of hydrogen.

Figure 3. Inner Oxide Layer Thickness as a Function of the Distance from the Cladding Defect (References 24, 25)

3.2.4 - Fuel Corrosion Properties

The relationship between in-pile fuel oxidation and internal cladding hydriding is that steam oxidation of fuel would be an additional source of free hydrogen in the fuel-cladding gap of defected rods. Both in-pile and out-of-pile tests demonstrated that thorium and thorium-uranium fuels, when compared with uranium, uranium-zirconium, and uranium-plutonium fuels, exhibit slower fission product leaching, lower levels of released activity, and minimal fuel solution and attrition by the coolant (Reference 8, 18 through 27). Metallographic examinations confirmed oxidation of UO_2 , UO_2-ZrO_2 and UO_2-PuO_2 at pellet surfaces in defected fuel rods (References 18, 19, 21, 23, and 25). No experimental evidence of in-pile oxidation of ThO_2-UO_2 fuel was observed in defected rod irradiation test programs (References 18 and 19). However, oxidative attack on high uranium (≥ 20 w/o UO_2) ThO_2-UO_2 pellets occurred in out-of-pile highly oxygenated water corrosion tests (References 18 and 27).

SECTION 4 - OUT-OF-PILE HYDRIDING TESTS IN H₂/H₂O GAS MIXTURES

As coolant enters the perforated cladding of an in-pile defected rod, the resulting steam atmosphere becomes enriched in hydrogen due to the Zircaloy corrosion reaction, fuel oxidation, and radiolytic decomposition of H₂O vapor in the fuel-cladding gap by recoiled fission products (References 8 and 28). A substantial number of out-of-pile hydriding tests were performed on Zircaloy specimens in H₂/H₂O atmospheres. The results indicated the existence of critical ratios of hydrogen to water vapor pressure (p_{H_2}/p_{H_2O}) above which massive hydriding occurred (References 25, 26, and 28 through 36). In order to gain some understanding of the changes taking place at the Zircaloy surface as the H₂O oxidant is depleted, Shannon (References 25, 26, and 29) measured the effect of gas atmosphere composition on the electrical properties of ZrO₂ corrosion films. The results revealed a large decrease in electrical resistance of ZrO₂ films when the atmosphere was changed from oxidizing to reducing. This was correlated with the initiation of massive hydriding and indicated a significant change in the morphology or defect structure of the oxide film (Reference 25).

Where the pickup rate of hydrogen in Zircaloy increases drastically, critical H₂/H₂O ratio values vary over a wide range. It was suggested (Reference 26) that in the presence of a significant pressure of hydrogen, the absolute pressure of the oxidant H₂O is the critical quantity controlling the potential for massive hydriding rather than the H₂/H₂O ratio. Other evidence indicates that the protective H₂/H₂O ratio is a function of the hydrogen partial pressure. Zima (References 24, 25, and 32) assessed experimental data on pre-filmed Zircaloy-2 coupon specimens over the 572 to 752F temperature range and developed the equations,

$$\log (p_{H_2}/p_{H_2O}) = 6 (p_{H_2})^{2/3} \quad (1)$$

$$(p_{H_2})_{\text{protective}} \geq 0.2 (p_{H_2})^{1/3} \quad (2)$$

defining limiting conditions under which protection may be lost. In either case, whether the controlling factor is the absolute H₂O pressure or the hydrogen partial pressure, the experimental data indicate that massive hydriding is favored when the supply of H₂O oxidant available to continuously repair

the protective zirconium oxide surface film falls below a critical value. Critical p_{H_2}/p_{H_2O} ratios were calculated as a function of hydrogen partial pressure with Zima's correlation. The calculated values (Tables 1 through 4) were compared with currently available experimental test results.

4.1 - ZIRCALOY ROD AND CAPSULE TESTS

In an attempt to simulate in-pile Zircaloy cladding hydriding failures, Boyle and Kisiel (Reference 31) corrosion tested 12 defected PWR-type, Zircaloy-2-clad fuel rods containing UO_2 fuel pellets in a steam-hydrogen atmosphere (100 psi H_2 /2000 psi steam). Four lengths of open tubing of the same Zircaloy stock were tested concurrently as control specimens. The 10.25-inch long rods were defected by drilling a 5-mil diameter hole through the cladding at a distance of 0.750 inch from the end cap. After 51 to 54 days of corrosion testing, cladding sections were cut from the ends, quarter points, and midpoints of six defected rods and one open tube. Segments for hydrogen analysis and metallography were taken from one end of the three remaining open tubes.

The results for the extreme cases are shown in Figures 4 and 5. As expected in an isothermal corrosion test, relatively uniform inside and outside surface oxide film thicknesses were measured* (Figure 4). The cladding total hydrogen content peaks between the center and third quarter of the rod, away from the defect end (Figure 5).

Since there were no temperature gradients along the length of the fuel rods and the oxide film thicknesses were relatively uniform, the data suggest an enrichment of hydrogen in the steam atmosphere of the annular space between the fuel and cladding. Corrosion takes place with accelerated hydriding occurring at regions removed from the defect hole as the p_{H_2}/p_{H_2O} ratio is increased.

* The inside film thicknesses are higher than the corresponding outside values. The difference is attributed to the superior surface cleanliness of the outside of the tubes (Reference 31).

Table 1 - Hydriding of Zircaloy-2 Rods and Capsules in H₂-H₂O Gas Mixtures

Geometry	Surface Condition	Temperature (°F)	Time (Hrs)	P _{H₂} (mm)	Calculated		Observation	Reference
					Measured P _{H₂} /P _{H₂O}	Critical P _{H₂} /P _{H₂O} *		
Defected Fuel Rod	Prefilmed	750	1224	5.2x10 ³	5x10 ⁻²	1.5x10 ³	Normal corrosion and accelerated hydriding	30
Capsule	Nonoxidized	608	40	760	1.25x10 ³	4.2x10 ²	No massive hydriding	32
Capsule	Nonoxidized	604	21	760	2.0x10 ³	4.2x10 ²	Massive hydriding limited to end cap crevice regions	32
Capsule	Nonoxidized	608	12	760	3.3x10 ³	4.2x10 ²	Massive hydriding in crevice regions	32
Capsule	Nonoxidized	590	6	760	>10 ⁷	4.2x10 ²	Massive hydriding distributed uniformly along crevice	32

* (P_{H₂O}) protective $\approx 0.2 (P_{H_2})^{1/3}$

Table 2 - Hydriding of Zircaloy-2 Tubing and Spheres in H₂-H₂O Gas Mixtures

Geometry	Surface Condition	Temperature (°F)	Time (Hrs)	p _{H₂} (mm)	Calculated		Observation	Reference
					Measured p _{H₂} /p _{H₂O}	Critical p _{H₂} /p _{H₂O} *		
Tubing	Nonoxidized	572	6	760	10 ³ -10 ⁴	4.2x10 ²	Accelerated hydriding	33
Tubing	Nonoxidized	572	6	760	10 ⁵ -10 ⁶	4.2x10 ²	Massive hydriding	33
Tubing	Nonoxidized	752	6	760	10 ² -10 ³	4.2x10 ²	Accelerated hydriding	33
Tubing	Nonoxidized	752	6	760	10 ⁴	4.2x10 ²	Massive hydriding	33
Tubing	Nonoxidized	1832	0.17	300	4x10 ⁻¹	2.3x10 ²	Accelerated hydriding (≤ 1250 ppm)	33
Tubing	Nonoxidized	2012	0.25	150	2.5x10 ⁻¹	1.4x10 ²	Accelerated hydriding (≤ 2250 ppm)	34
Tubing	Prefilmed	750	1296	5.2x10 ³	5x10 ⁻²	1.5x10 ³	Normal corrosion hydriding	30
Sphere	Prefilmed	650	144	760	10 ⁸	4.2x10 ²	No massive hydriding	30
Sphere	Prefilmed	650	264	8.8x10 ⁴	10 ⁴	9.9x10 ³	No hydriding observed	30

* (p_{H₂O}) protective ≈ 0.2 (p_{H₂})^{1/3}

Table 3 - Hydriding of Zircaloy-2 Coupons in H₂-H₂O Gas Mixtures

Surface Condition	Temperature (°F)	Time (Hrs)	p_{H_2} (mm)	Calculated		Observation	Reference
				Measured p_{H_2}/p_{H_2O}	Critical $p_{H_2}/p_{H_2O}^*$		
Vapor-blasted	752	72	0.1	1	1.1	No hydriding	28
Vapor-blasted	752	72	1	10	5	Normal corrosion hydriding	28
Vapor-blasted	752	232	5	50	17	Accelerated hydriding (775 ppm)	28
Vapor-blasted	752	48	10	10 ²	25	Accelerated (≤ 600 ppm) to massive hydriding	28
Vapor-blasted	752	6	10	2x10 ³	25	Massive hydriding to a powder	28
Prefilmed	752	168	68	66.7	85	Accelerated hydriding (580 ppm)	28
Vapor-blasted	752	2	10	17	25	Normal corrosion hydriding	31
Etched	752	2	10	17	25	Normal corrosion hydriding	31
Vapor-blasted	752	2	10	2x10 ³	25	Massive hydriding	31
Vapor-blasted	752	504	53	66	71	Evidence of hydriding	31
Etched	752	504	53	66	71	Evidence of hydriding	31
Autoclaved	752	504	53	66	71	Normal corrosion hydriding	31

* $(p_{H_2O})_{\text{protective}} \approx 0.2 (p_{H_2})^{1/3}$

Table 3 (Cont) - Hydriding of Zircaloy-2 Coupons in H₂-H₂O Gas Mixtures

Surface Condition	Temperature (°F)	Time (Hrs)	pH ₂ (mm)	Calculated		Observation	Reference
				Measured pH ₂ /pH ₂ O	Critical pH ₂ /pH ₂ O*		
Etched	752	504	29	3.6x10 ²	48	Evidence of Hydriding	31
Autoclaved	752	504	29	3.6x10 ²	48	Normal corrosion hydriding	31
Autoclaved	752	168	400	17	2.7x10 ²	Normal corrosion hydriding	31
Etched	662	1008	0.4	5	2.7	Normal corrosion	31
Etched and autoclaved	662	1008	0.4	5	2.7	Normal corrosion hydriding	31
Etched, autoclaved, scratched	662	1008	0.4	5	2.7	Normal corrosion	31
Etched	572	1008	0.4	5	2.7	Normal corrosion hydriding	31
Etched and autoclaved	572	1008	0.4	5	2.7	Normal corrosion hydriding	31
Etched, autoclaved, scratched	572	1008	0.4	5	2.7	Normal corrosion hydriding	31
Nonoxidized**	1382	11.7	20	2	40	Normal corrosion hydriding	29
Nonoxidized**	1382	11.7	50	5	70	Accelerated hydriding	29

* (pH₂O) protective = 0.2 (pH₂)^(1/3)

** 30-mil rolled strip

Table 3 (Cont) - Hydriding of Zircaloy-2 Coupons in H₂-H₂O Gas Mixtures

Surface Condition	Temperature (°F)	Time (Hrs)	p_{H_2} (mm)	Calculated		Observation	Reference
				Measured p_{H_2}/p_{H_2O}	Critical $p_{H_2}/p_{H_2O}^*$		
Prefilmed	650	168	7.6×10^2	10^5	4.2×10^2	No massive hydriding	30
Prefilmed	650	168	7.6×10^2	10^6	4.2×10^2	Some massive hydriding	30
Prefilmed	650	0.2	7.6×10^2	10^8	4.2×10^2	Massive hydriding	30
Prefilmed**	932	72	7.6×10^2	10^4	4.2×10^2	No massive hydriding	30
Prefilmed**	932	0.02	7.6×10^2	10^5	4.2×10^2	Massive hydriding	30
Etched	650	24	7.8×10^4	3.0	9.1×10^3	Accelerated hydriding (226 ppm)	30
Prefilmed	650	24	7.8×10^4	3.0	9.1×10^3	Accelerated hydriding (205 ppm)	30
Etched	650	24	9.0×10^4	3.5×10^1	1.0×10^4	Accelerated hydriding (193 ppm)	30
Prefilmed	650	24	9.0×10^4	3.5×10^1	1.0×10^4	Accelerated hydriding (206 ppm)	30
Prefilmed	650	24	6.2×10^4	3.8	7.8×10^3	Accelerated hydriding (234 ppm)	30
Prefilmed	750	720	2.6×10^4	3×10^{-1}	4.4×10^3	Normal corrosion hydriding	30

* $(p_{H_2O})_{\text{protective}} \approx 0.2 (p_{H_2})^{1/3}$

** coupons and chips

Table 4 - Hydriding of Zircaloy-4 Coupons in H₂-H₂O Gas Mixture

Surface Condition	Temperature (°F)	Time (Hrs)	p_{H_2} (mm)	Calculated		Observation	Reference
				Measured p_{H_2}/p_{H_2O}	Critical $p_{H_2}/p_{H_2O}^*$		
Prefilmed*	752	168	68.0	66.7	85.0	Normal corrosion hydriding (25 ppm)	28
Prefilmed	752	168	68.0	66.7	85.0	Normal corrosion hydriding (28 ppm)	28
Prefilmed	752	72	8.8×10^4	2×10^3	9.9×10^3	Accelerated hydriding (≤ 500 ppm)	***
Prefilmed	752	72	8.8×10^4	1×10^4	9.9×10^3	Massive hydriding but sample remained intact	***
Prefilmed	752	72	8.8×10^4	$> 1 \times 10^4$	9.9×10^3	Massive hydrid- ing to a powder	***

* Low nickel Zircaloy-2

** (p_{H_2O}) protective $\approx 0.2 (p_{H_2})^{1/3}$

*** Bettis Laboratory data

Figure 4. Variation in Corrosion Film Versus Length Along Rod. Total 54 Days Corrosion at 750F in 2000 psi Steam and 100 psi Hydrogen (Reference 31)

Figure 5. Distribution of Hydrogen as a Function of Length Along Rod or Tube. Total 51 Days at 750F in 2000 psi Steam and 100 psi Hydrogen Plus 3 Days at 750F in 1700 psi Steam (Reference 31)

These defected fuel rod results are compared in Table 1 with corrosion-tested Zircaloy-2 capsules (Reference 33). The capsules were tested at temperatures between 590 and 608F with the hydrogen-water vapor atmosphere flowing through their interiors. In the defected rods, the experimental p_{H_2}/p_{H_2O} ratios were considerably below the calculated critical ratio; and no massive hydriding occurred. The vapor pressure ratios of the capsule test atmospheres exceeded the calculated critical ratio. In three out of four cases, massive hydriding was observed.

4.2 - ZIRCALOY TUBING AND SPHERE TESTS

Results from hydrogen-steam testing of Zircaloy-2 tubing and solid spherical samples are compared in Table 2. The effects of geometry, surface condition, and test temperature are clearly evident. For the nonoxidized tubing specimens, massive hydriding occurred in a relatively short time period when environment p_{H_2}/p_{H_2O} ratios appreciably exceeded the calculated critical ratio. Also, the ratio at which massive hydriding occurred decreased with increasing temperature. In the case of the prefilmed spheres, neither accelerated nor massive hydriding was observed although the p_{H_2}/p_{H_2O} ratios exceeded the calculated critical ratios and the tests were of longer duration than the nonoxidized tubing tests. Thus, autoclaved oxide films on spherical Zircaloy specimens appear to have provided superior protection against accelerated and massive hydriding.

4.3 - ZIRCALOY COUPON TESTS

Most out-of-pile hydriding tests of Zircaloy in H_2/H_2O atmospheres were performed on coupons and on chip specimens (References 29, 30 through 32). Stresses in the oxide film at the edges of coupons and chips are more severe than in the surface films of tubing and spherical samples. This tends to result in earlier mechanical and chemical breakdown of the protective film when exposed to a hydriding atmosphere (References 26 and 31). Hydriding, often premature, was initiated at the sharp corners and edges of the Zircaloy coupons (References 6, 31, and 36). The effect of Zircaloy surface condition on hydrogen pickup can be observed from the hydriding test data on Zircaloy-2 coupons presented in Table 3. In agreement with studies in pure hydrogen

atmosphere, the surface films can be listed in the following order of decreasing protection: prefilmed/autoclaved > etched > vapor blasted. (References 6, 36, and 37). In some tests, even scratched autoclaved surfaces were protective in the H_2 - H_2O atmospheres. In contrast, accelerated and heavy localized hydriding were produced in etched Zircaloy surfaces by scratching the room temperature film and exposing the samples to pure hydrogen (Reference 6 and 36).

Less extensive data on Zircaloy-4 coupons is given in Table 4. In general, when experimental p_{H_2}/p_{H_2O} ratios were below the calculated critical values, normal corrosion hydriding occurred. In tests where p_{H_2}/p_{H_2O} ratios approached the calculated critical ratios, accelerated hydriding was observed. When measured ratios exceeded the critical ratios, the coupons massively hydrided.

4.4 - SUMMARY OF TEST DATA

A comparison of the test data listed in Tables 1 through 4 helps clarify the reasons for the widespread variations in the critical p_{H_2}/p_{H_2O} ratios reported in the literature (References 25, 26, 28 through 35). Specimen characteristics such as geometry and surface condition, as well as environmental factors such as hydrogen pressure, test temperature, and test time, affect the amount of hydrogen pickup. In addition, the type of Zircaloy (i.e., 2 or 4), the heat treatment, and minor variations in the alloying additions were also found to influence hydrogen absorption (References 38 and 39). These properties and their influence on hydriding are summarized in Table 5. Because of the many variables influencing hydriding, the data in Table 5 indicates that it is difficult to precisely predict the amount of hydrogen pickup in Zircaloy.

Table 5 - H₂-H₂O and H₂ Out-Of-Pile Test Summary

Property	Hydrogen Pickup
Specimen Geometry	Coupons > tubing > spheres
Zircaloy Surface	Abraded > etched > prefilmed
Type of Zircaloy	Zircaloy-2 > Zircaloy-4
Heat Treatment	α > β *
Test Temperature	As T ↑, [H ₂] ↑
Test Time	As t ↑, [H ₂] ↑
Hydrogen Pressure	As p _{H₂} ↑, [H ₂] ↑
H ₂ O Oxidant	As [oxidant] ↓, [H ₂] ↑

* Quenched from the β region.

SECTION 5 - FACTORS AFFECTING INTERNAL HYDRIDING IN DEFECTED ZIRCALOY FUEL RODS

5.1 - INTENTIONALLY DEFECTED VERSUS IN-PILE OPERATIONALLY DEFECTED RODS

The irradiation test data on defected Zircaloy fuel rods (References 7 through 15, 19, 21, 25, and 28) can be summarized as follows:

1. Intentionally defected test rods usually exhibited expected hydriding due to corrosion or accelerated hydriding rather than massive hydriding behavior.
2. Rods that operationally defected in-pile most often exhibited massive hydriding (unless operation was terminated shortly after the defect occurred).

The internal cladding surface of an initially undefected operating fuel element is similar to that of out-of-pile tests on bare Zircaloy since any prior oxide film (air or acid-etched) was dissolved or greatly reduced in thickness by the preirradiation fuel rod corrosion treatment and initial reactor operating temperatures (Reference 6). When Zircaloy cladding is initially breached, hot coolant flows through the defect into the fuel-cladding gap and migrates over the internal surface of the unprotected cladding at a flow rate determined by the difference between the outside coolant pressure and the internal pressure of the undefected fuel rod, the size of the fuel-cladding gap, and the size of the defect. Defects which occur in-pile are generally very small ($\ll 1$ mil) initially (References 8, 22, 24, 25, and 40). The rate of ingress through these operationally formed pinholes or cracks would be small relative to that through intentionally-fabricated (5-mil diameter) defect holes which are too large to duplicate the slow ingress rate of coolant through an operational defect (Reference 40).

Intentionally fabricated defected fuel rods, with their relatively large (5 mils and larger) defect holes, are less likely to massively hydride since sufficient oxidant can be present at all times during operation. Cold water enters the fuel-cladding gap at startup, flashes to steam at operating temperature, and causes formation of a protective oxide film over the internal

surface of the cladding. In addition, the penetration will permit equalization of pressure in the gap with external pressure of the coolant and thereby eliminate any tendency for progressive creep collapse of the cladding. Thus, tightly closed fuel-cladding gap areas, which would inhibit the flow of steam, should not occur in defected rods until later in life when the gap could be closed by fuel swelling alone or by partial blockage of the gap by corrosion products or fuel.

Also, coolant flow through a relatively large (≥ 5 mils) defect could replenish the oxidant depleted by corrosion such that the critical p_{H_2}/p_{H_2O} ratio is not exceeded. Power cycling could cause the pellet-cladding gap to be flushed, thereby inhibiting formation of the critical p_{H_2}/p_{H_2O} ratio if the time between cycles is less than the time required for the critical ratio to be achieved. In contrast, the smaller hole occurring in operationally defected rods will reduce the change in the p_{H_2}/p_{H_2O} ratio per cycle, which in turn reduces the time required to decompose the new atmosphere to the critical hydride-promoting p_{H_2}/p_{H_2O} ratio. A combination of small, operationally occurring defect and relatively steady, cycle-free mode of power operation would result in low coolant interchange, and the inside Zircaloy surface would receive little hydrogen flushing or H_2O oxidant replenishment, both of which inhibit hydriding.

5.2 - DEFECT SIZE

Small pinholes or cracks in operationally defected fuel rods do not always lead to excessive hydriding. It has been shown that defects can reseal themselves with corrosion products shortly after cladding breach with little or no hydride damage (References 22, 40, and 41). Some cladding cracks tightened and were too labyrinth-like to permit coolant penetration (Appendix A1). Other defected rods were identified only by the xenon and hydrogen found in the free volume of the rod by postirradiation fission-gas measurements (References 40 and 41).

Blockage and partial blockage of the 5-mil defect holes were observed in some of the intentionally defected LWBR irradiation test rods (Section 3.1.2). Using a computerized corrosion analysis procedure based on corrosion

and hydriding data from in-pile and out-of-pile Zircaloy tubing and designated CHORT, Corrosion and Hydriding of Reactor Tubing (References 7, 42 through 44), some representative corrosion calculations are listed in Table 6. The CHORT calculations show that a 5-mil hole can diminish in size in a reasonable length of time by oxide formation on the drilled surface of the hole.

It is also likely that operational in-pile defects will enlarge by crack extension or erosion (References 8, 22, 25, and 40). Theoretical analyses of the water/steam flow through a cladding defect were performed to classify various defect size ranges (Reference 40). The successive stages of hole deterioration are related qualitatively to the increase in coolant activity in Figure 6. Initially in Stage I, defects are detectable at about 10^{-3} mm (0.04-mil) to 10^{-2} mm (0.4-mil) diameter. The primary defect worsens through Stage I by erosion until, at Stage II, secondary hydriding defects start to penetrate the cladding. A transition in the coolant fission product activity level indicates multiple defect sites arising from enhanced secondary hydriding and major fuel loss can now occur (Stage III).

A relationship between defect size and hydrogen pickup was noted in out-of-pile burst tests on Zircaloy-4 rods containing Al_2O_3 pellets (Reference 45). The pressurized rods were heated in a steam atmosphere until they ruptured. Zircaloy hydrogen contents, analyzed at four rod positions, are compared with the size of the rupture openings in Table 7. Higher cladding hydrogen contents were associated with smaller size rupture openings which supplied less steam to the inner rod surface consistent with the qualitative models discussed above.

5.3 - SOURCES OF HYDROGEN

There are four possible mechanisms by which hydrogen can be generated in or introduced into a defected fuel rod: Zircaloy corrosion, radiolysis of water, fuel oxidation, and dissolved coolant hydrogen.

5.3.1 - Zircaloy Corrosion

Corrosion of zirconium alloys proceeds through the reaction

Table 6 - CHORT⁺-Calculated Oxide Growth at 5-Mil Defect Hole
Of Intentionally Defected LWBR Irradiation Test Rods

<u>Rod</u>	<u>EFPH</u>	<u>Oxide Thickness (mils)</u>
79-609D*	21,498	2.07
	25,886	2.49
	31,151	2.99
	35,898	3.45
79-443D*	3,707	0.74
	12,936	2.49
	15,349	2.96
	22,907	4.38
79-594D**	5,935	0.99
	17,627	2.49
	21,525	2.99
	27,535	3.77

+ Corrosion and Hydriding of Reactor Tubing

* 90 percent power position

** peak power position

Figure 6. Stages of Defective Fuel Rod Operation
Steady State (Reference 40)

Table 7 - Hydrogen Contents in Ruptured Zircaloy-4 Cladding*

<u>Burst Temperature (°F)</u>	<u>Size of Rupture Opening (in²)</u>	<u>Location 1</u>	<u>Location 2</u>	<u>Location 3</u>	<u>Location 4</u>	<u>Oxide Type</u>	<u>Oxide Structure</u>
1525	0.0004	2050	2200	2050	2000	Porous	Tetragonal and monoclinic
1600	0.0030	340	1230	1700	400	Porous	Tetragonal and monoclinic
1695	0.0033	570	860	810	500	Dense	Monoclinic
1635	0.0036	520	1650	178	111	Porous	Tetragonal and monoclinic
1435	0.0404	80	70	120	60	Dense	Monoclinic

*Reference 45

At the start of the oxidation process, all of the hydrogen may be absorbed (Reference 38). The rate of absorption steadily decreases from a maximum during the first 10 mg/dm² oxidation to a typical plateau value. Although the pickup fraction* of Zircaloy-2 depends somewhat on the oxygen content of the water or steam (Reference 39), it is usually between 10 percent and 50 percent (Reference 46). Zircaloy-4 has a pickup fraction between 5 percent and 25 percent. The hydrogen that is not absorbed is released to the fuel-cladding gap, thus enriching the steam atmosphere in hydrogen.

5.3.2 - Radiolysis of Water

It was proposed (Reference 28) that fission product radiolysis alters the steam/hydrogen ratio in two ways:

- a. Hydrogen is produced directly by radiolysis,

and,

- b. The energetic H₂O₂ molecule equilibrates with fuel in the presence of a large excess of hydrogen,

where ϵ is a small quantity and in the limit as $\epsilon \rightarrow 0$, i.e., the contact is between a large amount of fuel and a limited amount of oxidant.

Thermodynamic calculations (Reference 28 and Appendix A2) indicate that reaction (5) can proceed in the presence of a large hydrogen excess for both thorium and uranium fuels. The production of hydrogen by fission-product radiolysis is not an equilibrium-governed process because the rate of formation of hydrogen and hydrogen peroxide greatly exceeds their radical-induced

* Also called "hydrogen uptake" by some writers: the hydrogen absorbed by base metal during corrosion divided by total hydrogen liberated by the corrosion process.

recombination rate (Reference 28 and Appendix A2). As radiolysis and hydrogen production proceed, the peroxide molecules tend to react with fuel, generating still more hydrogen. The direct production of hydrogen by radiolysis and its further production from the peroxide-fuel reaction could contribute appreciably to increasing the hydrogen-water ratio.

5.3.3 - Fuel Oxidation

Although UO_2 is oxidized in a steam atmosphere, a very small concentration of hydrogen can retard the reaction (Reference 28 and Appendix A2). To the extent that the thermodynamic data are reliable, low urania ThO_2 - UO_2 compositions appear resistant to steam oxidation (Appendix A2). However, the more reactive peroxide molecule can oxidize both fuels in the presence of considerable hydrogen.

5.3.4 - Dissolved Coolant Hydrogen

The coolant in pressurized water reactors contains some dissolved hydrogen (10-60 cc/kg). It was calculated that this amount of hydrogen would make less of a contribution than radiolytically produced hydrogen to internal hydriding of the cladding (Reference 28).

5.4 - ZIRCALOY SURFACE PROPERTIES

5.4.1 - Surface Treatments

The role of Zircaloy surface treatment and surface film in hydrogen permeation was reviewed in Reference 6. An optically transparent oxide film is readily formed on the Zircaloys in air at room temperature. Chemical etching (HNO_3/HF) followed by atmospheric exposure results in the formation of transparent oxide films. The pickled film is more hydrogen-resistant than the room temperature air film on machined surfaces. Raising the hydrogen reaction temperature and increasing the time at temperature render these protective films more permeable to hydrogen.

5.4.2 - Corrosion Oxide Films

Incubation times observed before initiation of the hydriding reaction were longer with increasing zirconium oxide film thickness (Reference 34).

The type and morphology of the oxide were also related to hydrogen absorption (Reference 45). X-ray diffraction analyses showed that porous thicker oxide with higher hydrogen contents consisted of monoclinic and metastable tetragonal zirconia (Table 7). Denser, thinner oxide layers with less hydride consisted of monoclinic zirconia alone.

Two mechanisms were postulated to explain how zirconium oxide films permit hydrogen penetration. Mechanical defects such as microcracks, pores, intermetallic particle sites, as well as subgrain boundary and dislocation networks were proposed as short circuit paths in the oxide corrosion film through which hydrogen can come in contact with the zirconium substrate (References 47 and 48). A second mechanism relates hydrogen solubility and diffusivity through the oxide film to the presence of substoichiometry which permits more rapid movement of hydrogen through the oxygen vacancies (References 39, 47, and 48). By this mechanism, very thin films or those formed under reducing conditions are substoichiometric and, hence, hydrogen permeable; whereas water-formed films of normal thickness or those formed under oxidizing conditions are less permeable (Reference 39). Actually both mechanisms may operate simultaneously: hydrogen permeates through areas where the oxide film is substoichiometric and gaseous hydriding occurs in pores and cracks where the oxidant supply is limited.

5.4.3 - Fission Product Attack

Bombardment of the protective zirconium oxide film by highly energetic and relatively massive fission fragments could damage its resistance to hydrogen penetration (References 8, 22, 25 and 26). In addition, aggressive fission products such as iodine can react with the Zircaloy cladding (References 8, 25, 49 through 51):

In a defected rod, further reactions may take place:

These reactions release additional hydrogen for hydriding, are self-sustaining, and should continue until the iodine is leached out or a protective ZrO_2 layer is built up.

5.5 - NICKEL ALLOY CONTAMINATION

Two of the LWBR intentionally defected seed-type irradiation test rods, GRIP-II 79-441D and GRIP-IIIB 79-609D, had areas of accelerated and massive hydriding in their plenum regions (Reference 7). Cladding humps (1-4 mils in height) in the plenum region were measured on both rods. Metallographic examination of both rods revealed massive hydriding at the cladding humps. Cladding cracks emanating from the inside surface and through-wall cracks were also observed (Figure 2). Most of the cracks were covered and/or filled with zirconium oxide, indicating that the cracks occurred during the irradiation testing.

Electron microprobe examination of rod 79-609D identified Inconel X-750 constituents (Ni, Cr, Fe, and Ti) on the hydrided inside cladding surface. It was established through out-of-pile testing (References 52 and 53) that Inconel-600 from LWBR fuel module baseplates can smear and mechanically bond to the bearing surfaces of Zircaloy-4 LWBR fuel element rod and connector nuts due to torquing during module assembly. The nickel-alloy smearing resulted in subsequent accelerated hydriding on exposure to LWBR coolant conditions. A model developed for analyzing the hydriding in LWBR end connector nuts proposes that nickel-bearing alloy be smeared and bonded onto the surface of a Zircaloy component with disrupted or damaged oxide film (or without an oxide film). It then becomes permeable to hydrogen dissolved in the coolant water and thereby acts as a window allowing the ingress of hydrogen to the Zircaloy (Reference 52).

In the hydrided intentionally defected seed fuel rods, Inconel transfer could occur through rubbing of the plenum spring due to the relative motion

caused both by fuel-cladding elongation associated with power swings and by any rod vibration during operation. If bonded to the Zircaloy metal surface, the transferred Inconel could increase the hydrogen ingress rate and accelerate the hydriding process. The nickel contents of Inconel-600 (76 wt %) and Inconel X-750 (70 wt % minimum) are similar although the latter alloy is harder and should smear less.

In some LWR-related Bettis out-of-pile tests, Inconel X-750 springs were inserted into 12-inch long seed-size Zircaloy-4 tubes and compressed for 200 and 2000 cycles. Scanning electron microscopy and electron microprobe examination of the cladding surfaces for Inconel transfer were then performed. Both techniques detected a sparse population of small nickel-rich contamination spots on the inner Zircaloy cladding surfaces. The spots had the composition of Inconel X-750. These findings demonstrate that some Inconel transfer can occur by rubbing Inconel X-750 plenum springs against Zircaloy-4 cladding. They are in agreement with the results of electron microprobe examination of GRIP-IIIB rod 79-609D where Inconel X-750 constituents (Ni, Cr, Fe, and Ti) were detected on the hydrided inside cladding surface. Since nickel-alloy smearing and bonding, rather than just tight-surface contact and nickel transfer, are necessary for accelerated hydriding (References 52 and 53), these test results are insufficient to clarify the role of Inconel contamination in the hydriding of defected LWR Zircaloy seed fuel rods.

It was observed that the plenum regions of the two LWR defected test rods were not uniformly hydrided but that heavy hydriding and cladding humps occurred only at specific points, presumably where the spring contacted the cladding. Further evidence for the role of nickel contamination and bonding from the Inconel plenum spring was demonstrated for rod 79-609D by neutron radiographs which showed that the plenum spring contacted the cladding inside surface at exactly the elevation and circumferential position of the major cladding hump. The position of the major cladding hump was determined from axial diameter traces and from the appearance of a white spot on the neutron radiograph, typically observed at heavily hydrided regions, at the exact position of plenum spring contact with the cladding inside surface.

A cladding hydrogen content of 100 ppm was measured at a zero power position just below the plenum of rod 79-609D. This indicates that axial thermal diffusion of hydrogen within the cladding was negligible and is in agreement with hydrogen diffusion calculations (Reference 7). These results together with out-of-pile defected rod test data of Reference 31 (Section 4.1) suggest that hydrogen was transported by diffusion to end regions of the defected rods in the gaseous state via the fuel-cladding gap. Excessive hydriding then occurred as a result of the window for ingress of hydrogen formed by the pick-up and bonding of nickel due to rubbing of the Inconel X-750 plenum spring.

Inconel-induced hydriding would be unlikely, and was not observed, in defected LWBR blanket test rods because of the Type 348 stainless steel support sleeves surrounding the springs in blanket plenums (Reference 17). The nickel content of Type 348 stainless steel is 9-13 wt %, and there is little relative motion between the support sleeve and the cladding surface.

The hydriding mechanism based on hydrogen overpressure, as developed in Section 6 of this report to explain excessive hydriding in defected Zircaloy rods, is compatible with and could also account for the high hydrogen contents in the defected seed rods without Inconel-induced acceleration. In addition, only the hydrogen overpressure mechanism (discussed in Section 6) could explain the massive hydriding observed at the bottom end away from the defect hole and remote from the plenum spring in LWBR operationally defected blanket irradiation test C7-B3A rod 79-353.

5.6 - EFFECT OF HEAT FLUX

Locke has developed an empirical approach for determining fuel rod lifetime after fuel rod defects occurred (References 8, 22, 25, and 40). He correlates the period of time a defected rod can operate in-pile before failure with the Zircaloy cladding surface heat flux. The permissible operating time periods decreased, and accelerated and massive hydriding increased at the higher heat fluxes. Surface heat flux determines both the cladding radial thermal gradient and the inside cladding temperature for a given geometry and coolant temperature. Heat flux is a direct function of the fission rate in the fuel. Locke compiled the available in-pile data up to 1979 (including

some Bettis Laboratory data) on both intentionally and operationally defected Zircaloy-clad fuel rods. As shown in Figure 7, he drew a limit line on the plot of the rod surface heat flux versus days to failure after cladding breach. The conclusion was that the limiting levels of operation are about 120 to 150 w/cm² (380,000 to 475,000 BTU/hr-ft²) peak flux at a coolant temperature of 500 to 626F, should it be desirable to operate with defected fuel rods for an extended period of time.

5.7 - EFFECT OF FLUENCE

Initial test data on water corrosion of Zircaloy indicated that in-pile corrosion and associated hydriding was only slightly higher than the out-of-pile behavior (References 25, 39, 54, and 55). However, more and more enhanced Zircaloy corrosion and hydrogen pickup was observed as in-reactor residence times continue to increase (References 43, 44, 56 through 58). Irradiation-induced corrosion enhancement of Zircaloy was observed to decrease with increasing temperature. There is experimental evidence that the accelerated corrosion and hydriding is at least partly due to fast neutron damage of the protective oxide layer (Reference 59). The decrease in the enhancement factor with increasing temperature can be explained as due to the progressive annealing of irradiation damage (Reference 60). Increased inner cladding surface corrosion and total hydrogen content in defected Zircaloy fuel rods was attributed to a combination of irradiation enhancement, higher inside cladding temperatures, and surface fissioning enhancement caused by the proximity of the oxide fuel pellets (References 7, 61, and 62).

In PWR systems where there was either deliberate or inadvertent additions of oxygen to the coolant, the presence of fast neutron flux (or fluence) produced a pronounced enhancement of the Zircaloy corrosion rate. However, when the oxygen content in the coolant was high, a very dramatic reduction in hydrogen pickup was produced. Smaller oxygen contents resulted in only minor decreases in hydrogen absorption (References 5 and 55).

Figure 7. Hydride Failure Limit for Defected Zircaloy-Clad Fuel Rods (Reference 40)

SECTION 6 - DESCRIPTIVE MODEL FOR SECONDARY HYDRIDING IN DEFECTED ZIRCALOY CLAD FUEL RODS

This model is based on a mechanism first proposed by Markowitz (Reference 28) and refined by later workers (References 8, 22, 25, and 40). Most current mechanisms for hydriding in defected Zircaloy rods depend upon one common condition: the corrosive environment contains insufficient oxidizing power to maintain normal oxidation kinetics coupled with the presence of sufficient hydrogen to induce accelerated or massive hydriding of less-protected Zircaloy.

The proposed hydriding mechanism is as follows:

1. Coolant pressure outside an undefected fuel rod is usually much greater than internal pressure. Thus, when a rod defects in service, coolant enters the fuel rod to equalize pressure.
2. Hot coolant flows through the defect opening into the fuel-cladding gap and is vaporized to steam. Some coolant is radiolytically decomposed to hydrogen and peroxide.
3. As steam first passes over the internal Zircaloy cladding surface near the defect hole, this surface is oxidized to ZrO_2 , resulting in the release of > 75 percent of the hydrogen produced by the corrosion process. (The remainder of the hydrogen enters the cladding uniformly.)
4. The released hydrogen is carried along as the coolant gas flows farther over the internal surface. It moves at a flow rate determined by the pressure difference between outside coolant pressure and internal pressure of the undefected element, size of the fuel-cladding gap, and size of the defect hole.
5. Hydrogen gas from the cladding corrosion reaction is augmented by hydrogen produced by coolant radiolysis and fuel oxidation. Hydrogen from corrosion, radiolysis, and fuel oxidation combine to reduce the steam oxidant partial pressure.

6. As the gases (initially mainly steam) flow along the fuel-cladding gap, concentration of hydrogen is continually increasing. Representative changes in internal pressures of both steam and hydrogen, as the inner cladding surface is oxidized, are illustrated in Figure 8.
7. At peak power and heat flux position, the oxide layer formed is hottest and its self-healing properties are greatest. However, the cladding thermal gradient is highest at the peak heat flux positions, and thermal diffusion of any absorbed hydrogen to the outer cladding surface is greatest.
8. As the gas moves beyond peak power and heat flux positions, it becomes more enriched in hydrogen. Oxidation of the internal cladding surface is lessening, and any defects in the oxide film are less likely to heal.
9. If the rate of inflow of steam is sufficiently low and radiolysis, cladding, and fuel oxidation rates sufficiently high, or if hydrogen passes preferentially through a very small fuel-cladding gap, it is possible that at some point along the gas flow path a "critical ratio" of steam and hydrogen is produced which can cause high hydrogen pickup.
10. Conditions for accelerated hydriding and massive hydriding of localized areas may be achieved at some point along the internal Zircaloy cladding surface. Such hydriding could occur at a defect or discontinuity in the ZrO_2 skin or at a region where the protective oxide is thin. It would be remote from the defect hole and probably at a region past the peak power and maximum heat flux positions.
11. With removal of hydrogen from the internal gas atmospheres to the cladding and the movement of oxygen into the fuel and cladding, internal rod pressure must fall, allowing more coolant to enter through the defect. Within broad limits, coolant pressure drop must adjust to provide fresh coolant molecules at a rate equivalent to hydrogen consumption by hydriding. The effect of steam replenishment is to maintain a nonhydriding atmosphere in the vicinity of the defect.

Figure 8. Development of H₂O and H₂ Pressures in PCI Defected Fuel Rod (Reference 22)

12. At higher heat fluxes the temperature of the inner cladding surface is higher and the corrosion film will form more rapidly, depleting the environment of steam and approaching oxygen starvation conditions earlier.
13. At higher heat fluxes the environment tends to be more conducive to hydriding because equilibrium p_{H_2O}/p_{H_2} ratios is lower (p_{H_2}/p_{H_2O} ratios higher). Calculated p_{H_2O}/p_{H_2} ratios are plotted versus power for different O/U ratios in the fuel pellet in Figure 9.
14. The effect of released fission products is to accelerate the onset of localized hydriding by prematurely destroying the protective qualities of the ZrO_2 corrosion film.

Figure 9. Calculated H_2O/H_2 Ratio in a Fuel Rod Versus Power and Fuel O/U Ratio (Reference 22)

SECTION 7 - MINIMIZING SECONDARY HYDRIDE FAILURES

Frequency of fuel rod failures due to secondary hydriding of the internal Zircaloy cladding can be reduced by the following methods: prevention of primary hydriding, control of hydride orientation, protective coating of cladding inner surface, hydrogen getters, and power restrictions.

7.1 - PREVENTION OF PRIMARY HYDRIDING

Current fuel rod fabrication techniques have almost eliminated primary hydriding and thus reduced incidents of subsequent secondary hydriding. The most common causes of primary hydriding were contamination by moisture and organic residues (References 2, 5, 6, 26, 63 through 65). Since the total moisture pickup increases with increasing fuel pellet surface area and decreasing fuel density, primary hydriding was more prevalent in rods containing low density and vibratory-compacted fuel than in high density fuel pellet rods (References 1, 2, 5, 63, and 65). Pellet drying and hot vacuum degassing techniques were successfully applied as remedies for minimizing fuel rod moisture levels (References 1, 2, 5, 64, and 65).

In order to minimize the potential for primary hydriding in LWBR fuel rods, hydrogenous materials in the fuel rod were minimized by stringent controls on the manufacturing process (Reference 6). All LWBR production fuel pellets were of high density (95 percent theoretical density, or greater). After sintering and grinding, the pellets were vacuum degassed for 3-4 hours at 1832F and stored in a dry atmosphere until ready for loading into fuel rods. Randomly selected pellet samples were given an additional vacuum extraction treatment at 2912F for control purposes, and the evolved gases were measured and required to meet a product attribute limit. Manufacturing controls were placed on the humidity levels and exposure times of the pellets to air after vacuum outgassing.

Zircaloy-4 tubing and rod internal components were cleaned, rinsed, and vacuum dried prior to rod loading to minimize residual volatile gases. Finally, representative fuel rods were sampled for atmospheric purity after corrosion testing with the composition of acceptable rod internal atmosphere limited to 2 mole percent total impurities (including hydrogen derived from

all sources). The LWBR core operated for 29,047 EFPH; there was no detectable breach of the cladding in any of the 17,290 fuel rods.

7.2 - CONTROL OF HYDRIDE ORIENTATION

Early tests indicated that several hundred ppm of hydrogen, uniformly distributed in the Zircaloy cladding, can contribute to structural failure of a fuel rod by degrading its mechanical properties. Later studies concluded that Zircaloy becomes embrittled only if the hydride platelets precipitate in the radial direction, i.e., perpendicular to an applied tensile stress (References 5 and 66). By reducing the ductility of Zircaloy, radial hydrides in the cladding of an operating fuel rod act as crack initiation sites as they are oriented perpendicular to the hoop stresses in the cladding (Reference 5).

The hydride orientation is related to the texture of the Zircaloy, and this is dependent on the fabrication process. Drawing and sinking methods for manufacturing Zircaloy tubes yield a texture that leads to radially oriented hydrides. Fabrication processes like tube reduction, hot extrusion, and pilgering* yield a radial basal pole texture that leads to circumferentially oriented hydrides, i.e., parallel to an applied stress (Reference 5).

The methods for manufacturing LWBR cladding used major reductions in wall thickness rather than in diameter during the forming process. This resulted in textures which gave a high degree of hydride orientations in the circumferential direction. Detailed examinations of LWBR seed and blanket irradiated cladding specimens confirmed that the hydride platelets were circumferentially oriented.

7.3 - PROTECTIVE COATING OF CLADDING INNER SURFACE

Early tests used chemical etching and prefilmed Zircaloy inner surfaces to reduce hydrogen pickup in the cladding (References 5, 6, 36, and 37). Recently barrier fuel was developed as a solution to pellet-cladding interaction (PCI) fuel rod failures (References 67, 68, and 69). Several designs

* Pilgering is a process for fabricating seamless tubes that uses a grooved rolling mill that exerts a forging force on the piece.

(copper-barrier, zirconium-liner, graphite-coating) were evaluated through irradiation in commercial boiling water reactors and power ramp tests.

Copper-barrier rods are Zircaloy cladding tubes with a thin layer of copper plated on the inner surface. A zirconium oxide layer exists between the copper and the Zircaloy cladding to eliminate diffusion of copper into the Zircaloy matrix. In zirconium-liner rods, a layer of pure zirconium is metallurgically bonded to the Zircaloy cladding inner surface, forming an integral part of the cladding tube. The pure zirconium barrier constitutes approximately 10 percent of the cladding wall thickness. Graphite-coated rods have a layer of graphite between the Zircaloy cladding tube and the fuel pellet. The graphite coating is either on the pellet surface or the cladding inner surface. Since the barrier metals are softer than Zircaloy, they effectively prevent local applied stresses from exceeding the critical levels needed to propagate stress corrosion cracks and allow reactor operation with less restrictions on power increases. The benefit of the graphite coating may be due to several factors (Reference 70):

1. By acting as a lubricant, the graphite decreases the coefficient of friction between the oxide fuel and the Zircaloy cladding and thus reduces the stress concentration.
2. The graphite adsorbs or absorbs aggressive fission products such as iodine.
3. The graphite forms a physical barrier between the cladding and fission products released from the fuel.

7.4 - HYDROGEN GETTERS

Hydrogen getters by preferentially absorbing the hydrogen generated within a fuel rod can protect the Zircaloy cladding from hydrogen attack and prevent primary hydriding (References 1, 5, 25, and 26). Getters can also minimize secondary hydriding and improve the operational behavior of defected fuel rods (Reference 5). Getter materials for fuel rods should have low neutron absorption cross sections, an affinity for hydrogen that is much greater than that of Zircaloy, and the ability to absorb and retain a large

amount of hydrogen at temperatures higher than the cladding temperature of the operating fuel rod. Yttrium and zirconium metals and zirconium alloyed with titanium and aluminum were successfully tested in fuel rods as getters (Reference 5). A combination of an autoclaved inner cladding surface and a getter is particularly advantageous for reducing hydrogen pickup in Zircaloy rods.

7.5 - POWER RESTRICTIONS

As reported in Section 3.1.2, three intentionally fabricated defected and one operationally defected LWBR irradiation test rods acquired localized areas of accelerated and massive hydriding in their cladding and yet operated successfully for up to almost 20,000 EFPH (Reference 7). Excessive hydriding need not lead to cladding failure immediately but much later when sudden stresses occur from operations such as power ramps. A hydrided cladding may last for years without failure if there is no severe power cycling or load changes during operation (References 1, 5, and 25). After a reactor shutdown, a cautious mode of return to power is advisable to avoid waterlogging of any defected fuel rods. This could happen during a fast return to power if there is sufficient coolant water inside the defected rod to form steam which then bursts the rod by its high internal pressure. As discussed in Section 5.6, defected Zircaloy fuel rods can be operated without failure for additional lifetime as long as the cladding surface heat flux is kept within empirical limits.

SECTION 8 - SUMMARY OF REVIEW

1. Intentionally defected Zircaloy test rods usually do not excessively hydride.
2. Zircaloy fuel rods that defect in service generally acquire localized areas of accelerated or massive hydride.
3. Both intentionally and operationally defected fuel rods with local areas of accelerated and massive zirconium hydride can operate without failure for extended periods of time under restricted power conditions.
4. Out-of-pile zirconium hydriding test data in H_2/H_2O gas mixtures shows that specimen characteristics (geometry and surface conditions) as well as environmental factors (hydrogen pressure, test temperature, and test time) affect the amount of hydrogen pickup in Zircaloy. In addition, the type of Zircaloy (2 or 4), the heat treatment, and minor variations in the alloying conditions were also found to influence hydrogen absorption.
5. The significant factors affecting internal hydriding in defected Zircaloy rods are defect size, sources of hydrogen, Zircaloy cladding inside surface properties, aggressive fission product attack on inner oxide film, nickel alloy contamination of Zircaloy, and the effects of heat flux and fluence.
6. Pertinent in-pile and out-of-pile test data and the significant factors affecting internal hydriding in defected Zircaloy fuel rods are used as a data base in constructing a descriptive model which explains hydrogen distribution in Zircaloy cladding of defected water-cooled reactor fuel rods.
7. Methods for minimizing secondary hydride failures in defected Zircaloy fuel rods include control of hydride orientation, protective coatings, hydrogen getters, and power operating restrictions.

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SECTION 10 - ACKNOWLEDGMENTS

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APPENDIX A1

HYDROSTATIC TESTING OF IODINE STRESS CORROSION CRACKED ZIRCALOY TUBING

Ten Zircaloy-4 tubing specimens (five seed and five blanket) that were previously cracked with internal pressure loading in iodine stress corrosion cracking tests were studied to determine the leak rates at various internal and external hydrostatic pressures. The specimens are described in Table A1-1. The defects were located within a 4-inch long center section of the tubing specimens where the wall thickness was reduced to facilitate the iodine stress corrosion cracking.

Out-of-pile hydrostatic tests of these cracked, pressurized Zircaloy-4 tubing specimens could not detect any leaks prior to overpressuring the tubes to collapse. The cracks apparently tightened and were too labyrinth-like to permit any significant liquid flow when the differential pressures were such as to compress the tube.

The blanket tubes were externally pressurized for 10 to 60 minute periods in increments to 400 psi without any evidence of leakage. Blanket tube 98S suddenly collapsed and began to leak when the external pressure reached 450 psi. In a second test, the remaining four blanket tubes were externally pressurized to 350 psi for 6.5 hours. After 2 hours, tube 91S began to leak and eventually collapsed.

The five seed tubes were internally pressurized and held for 30 minutes at 50, 100, 300, 500, 700, 900, and 1000 psi without developing any leaks. Seed tube 135 was left in the test and held for 5 minutes at 1100, 1200, 1300, 1400, 1500, 1600, 1700, and 1800 psi, and 15 minutes at 1900 and 2000 psi without any leakage. The pressure was increased to 2100 psi and the seed tube began to leak at a rate of 1 psi per minute until the pressure decreased to 2080 psi at which point the leak stopped. The tube was held at 2080 psi for 10 minutes without any evidence of further leakage. A film of moisture was observed on the external surface of seed tube 135 on removal from the test apparatus. The hydrostatic test water temperatures varied from 70 to 86.5F.

Table A1-1 - Summary of Cracked Tubing Hydrostatically Tested

Specimen	Center Section Tube Wall Thickness (mils)	Original Evaluation of Defect	Evaluation of Defect After Hydrostatic Testing
<u>RXA Seed</u>			
102	12	Pinhole	Defect not visible at 30X.
135	12	Pinhole	Spots of discoloration on surface.
141	12	Pinhole	Axial defect 1/2" from bottom end.
152	12	Pinhole	Axial defect at bottom end.
153	12	Pinhole	Spots of discoloration overall.
<u>SRA Blanket</u>			
92S	16.8	Pinhole	Pit in weld on bottom end.
102S	12	Pinhole	Axial defect 2" from bottom end
94S	12	D (~20 mils)	Axial defect 3/4" from bottom end
91S	12	S (~30 mils)	Collapsed tube, axial defect 1 1/2" from bottom end
98S	12	D (~20 to 30 mils)	Collapsed tube, axial defect 1/2" from bottom end.

D = Deformed; failure is apparently an axial split, but no crack is visible.

S = Axial split; failure is visible crack with little deformation.

RXA = Recrystallization annealed.

SRA = Stress-relief annealed.

After the hydrostatic tests were completed, two specimens (blanket tube 94S and seed tube 152) were cross-sectioned and measured via as-polished metallographic enlargements to determine the dimensions of the defects and to investigate why the tubes did not leak. The defects in both tubes were approximately 30 mils long and the width varied from 0.3 mil to less than 0.1 mil. Both defects took an indirect path rather than going straight through the tubing.

APPENDIX A2

THERMODYNAMICS OF FUEL OXIDATION IN DEFECTED ZIRCALOY FUEL RODS

A2.1 - HYDROGEN GENERATION BY THE STEAM-FUEL REACTION

Sintered UO_2 and $\text{ThO}_2\text{-UO}_2$ fuel normally has an O/U ratio of about 2.01. The molecular formula for mixed fuels, however, is in the form $\text{U}_y \text{Th}_{1-y} \text{O}_{2+x}$ where $2+x$ is the oxygen-metal ratio, O/M. The relationship between the two ratios is $x = x' y$, where $x' = (O/U - 2)$ and $x = (O/M - 2)$. Thus, for $\text{ThO}_2\text{-6 m/o } \text{UO}_2$ with $O/U = 2.01$, the normal as-sintered composition has the formula

The reaction of steam (H_2O) with UO_{2+x} and $\text{U}_y \text{Th}_{1-y} \text{O}_{2+x}$ can be formulated as the following chemical equilibria (Reference 27)

where ϵ is a small quantity and in the limit as $\epsilon \rightarrow 0$, i.e., the contact is between a large amount of fuel and a limited amount of oxygen.

The sum of reactions I and II is the overall reaction

The equilibrium constants for these reactions are

$$(1) \quad K_I = \frac{(p_{H_2})^2 p_{O_2}}{(p_{H_2O})^2}$$

$$(2) \quad K_{II} = \frac{1}{p_{O_2}}$$

$$(3) \quad K_{III} = \frac{(p_{H_2})^2}{(p_{H_2O})^2}$$

In addition $K_I K_{II} = K_{III}$. These constants can be evaluated from the free energy of formation of water (Reference A2-1) and from the relative partial molar free energies of solution of oxygen in the fuel (References A2-2 through A2-4). The partial pressure of oxygen over fuel can be calculated from K_{II} . By assuming a total pressure of 100 atmospheres, the partial pressure of oxygen in equilibrium with isolated water vapor can be calculated. The results of such calculations are presented in Table A2-1. The thermodynamic calculations show that the equilibrium hydrogen-water ratios over both fuels are much lower than the out-of-pile critical ratios ($4.2 \times 10^2 - 1.5 \times 10^3$) listed in Table 1 as dryness criteria for Zircaloy rods and capsules. Therefore, if these criteria are valid in-pile, hydriding of the Zircaloy cladding by the steam-fuel oxidation mechanism is ruled out. The data of Table A2-1 further show that the equilibrium hydrogen-to-water ratios in pure water vapor and in water vapor generated from loop water are greater over almost all of the temperature range than the equilibrium ratios over the thorium-uranium fuel. This means that water vapor is actually reducing to fuel of this composition. In contrast, water vapor is oxidizing to UO_2 except at the lowest temperature shown.

Table A2-1 - Reaction III Thermodynamics*

Temperature °C	p_{H_2}/p_{H_2O} in Equilibrium with		O_2 at 100 Atm	
	$UO_{2.01}$	$U_{.06}Th_{0.94}O_{2.0006}$	Loop Water**	Pure Water
500	3.2×10^{-6}	4.0×10^{-10}	2.0×10^{-5}	1.7×10^{-10}
1000	2.4×10^{-3}	4.2×10^{-6}	3.9×10^{-5}	4.2×10^{-6}
1500	4.4×10^{-3}	1.8×10^{-5}	3.2×10^{-4}	3.2×10^{-4}
2000	2.2×10^{-1}	1.2×10^{-3}	2.5×10^{-3}	2.5×10^{-3}
2500	6.4×10^{-1}	5.1×10^{-3}	9.4×10^{-3}	9.4×10^{-3}

** 25 cc NTP/kg hydrogen added; molar ratio = 2×10^{-5}

A2.2 - HYDROGEN PRODUCTION BY FISSION PRODUCT RADIOLYSIS

It was proposed in Reference 28 that fission product radiolysis alters the steam-fuel-cladding interaction in two ways: (1) hydrogen is produced directly by radiolysis

at a sufficient rate to satisfy the hydrogen flux criterion, and (2) the energetic H_2O_2 molecule equilibrates with fuel in the presence of a large excess of hydrogen:

The equilibrium constant corresponding to reaction V is simply

$$\frac{p_{\text{H}_2}}{p_{\text{H}_2\text{O}_2}}$$

and was calculated over a wide temperature range (500-2500C). The thermodynamic calculations, given in Table A2-2, show that reaction V can proceed in the presence of a large hydrogen excess for both fuels. The production of hydrogen by fission-product radiolysis is not an equilibrium-governed process because the rate of formation of hydrogen and hydrogen peroxide greatly exceeds their radical-induced recombination rate (Reference A2-5). As radiolysis and hydrogen production proceeds, the peroxide molecules tend to react with the fuel, generating still more hydrogen. Thus, the direct production of hydrogen by radiolysis and its further production from the peroxide-fuel reaction could contribute appreciably to increasing the hydrogen-water ratio in defected Zircaloy fuel rods.

Table A2-2 - Reaction V Thermodynamics*

Temperature °F	$p_{H_2}/p_{H_2O_2}$ in Equilibrium with	
	$UO_{2.01}$	$U_{.06}Th_{0.94}O_{2.0006}$
500	7.9×10^{12}	1.15×10^5
1000	2.0×10^9	2.5×10^3
1500	5.5×10^7	5.1×10^2
2000	7.1×10^6	2.0×10^2
2500	1.7×10^6	1.05×10^2

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