

# ZIRAT-8 ANNUAL REPORT

*Prepared by*

Al Strasser,  
Aquarius Seivices Corp., NY, USA

Ron Adamson,  
Zircology Plus, Pleasanton, CA, USA

Brian Cox,  
University of Toronto, Ontario, Canada

Peter Rudling and Gunnar Wikmark,  
Advanced Nuclear Technology Sweden AB, Sweden

**December, 2003**

Advanced Nuclear Technology International

Ekbacken 33

SE-735 35 SURAHAMMAR

Sweden

[info@antinternational.com](mailto:info@antinternational.com)



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## EXECUTIVE SUMMARY

### 1-INTRODUCTION

The objective of the Annual Review of Zirconium Alloy Technology (ZIRAT) is to review and evaluate the latest developments in zirconium alloy technology as they apply to nuclear fuel design and performance.

The objective is met through a review and evaluation of the most recent data on zirconium alloys and to identify the most important new information and discuss its significance in relation to fuel performance now and in the future. Included in the review are topics on materials research and development, fabrication, component design, and in-reactor performance.

The extensive, continuous flow of journal publications is being monitored and relevant conferences are being covered. The data obtained from these sources are summarised and critically evaluated.

The primary issues addressed in the review and this report are zirconium alloy research and development, fabrication, component design, ex- and in-reactor performance.

Background data from prior periods have been included wherever needed. The information within the ZIRAT-8 Program is either retrieved from the open literature or from proprietary information that ANT International has received the OK from the respective organisation to provide this information within the ZIRAT-program.

The compilation, evaluations, and conclusions in this report are proprietary to ANT International and ZIRAT members as noted on the title page.

The authors of the report are Dr. Ron Adamson, Brian Cox, Professor Emeritus, University of Toronto; Al Strasser, President of Aquarius; Dr. Gunnar Wikmark, President of ANT and, Peter Rudling, President of ANT International.

The work reported herein will be presented in three Seminars: one in Lisbon on January 13-15, 2004 and one in Key Largo, Florida, on January 27-29, 2004 and one in Japan on March 29, 2004.

The Term of ZIRAT-8 starts February 1, 2003 and ends January 31, 2004.

In the following, the main conclusions from each of the 12 sections in the report are provided.

## 2-FUEL PERFORMANCE GOALS AND ACHIEVEMENTS

The deregulated market means that the nuclear utilities must reduce operating, maintenance and fuel cycle costs to remain competitive. Also reactor safety must be improved while the plant radiation build-up must be limited to cope with the change in political environment towards nuclear power. To achieve the above mentioned goals the following changes have been and are being introduced:

- Longer cycles. Longer cycles do not necessarily meet any of the goals noted above; they do however reduce licensing needs and save storage space. Two-year cycles start to be marginal in some cases economically.
- Higher discharge burnups,
- Modified water chemistries (e.g. elevated LiOH in PWRs, NMCA in BWRs, Zn-injection in BWRs and PWRs)
- Plant power uprates
- More aggressive fuel management methods

However there are a number of different issues that needs resolution to be able to successfully implement the above-mentioned changes. The most important issues are:

- Oxidation levels higher than predicted,
- Excessive internal gas pressure in burnable poison rods,
- Incomplete control rod insertion (IRI) events,
- Large axial offsets or axial offset anomalies (AOA),
- Fuel failures due to a combination of high duty, material properties and increasingly complex water chemistries,
- Adverse effects of water chemistry,
- High crud build-up, and
- Accelerated growth of rods and assemblies
- Grid fretting due to spring relaxation
- Potential effects of high burnups on clad properties and their effect on RIA, LOCA and BWR power oscillations (ATWS)

The fuel vendors on their part are developing new fuel designs, including more advanced materials to resolve some of the issues. It is important to keep in mind that the new alloys were initially developed solely to improve corrosion performance and that there may be some changes in the performance related to other material properties.

### 3-ZIRCONIUM ALLOY SYSTEM

The material performance in-reactor is a function of the reactor environment as well as the material microstructure. The microstructure depends on the chemical composition and the manufacturing process of the alloy. Characterisation of the material microstructure in relation to the material performance can elucidate the mechanisms behind the material performance. This knowledge can be used by fuel vendors to modify the manufacturing process to get optimum material performance in-reactor.

The main key results during 2003 are the following:

- Annealing Zr- 10Nb alloys in the temperature range from 570 to 600°C and subsequent SEM and TEM examinations suggest that the monotectoid temperature of the Zr-Nb binary alloy system is approximately 585°C<sup>1</sup>.
- The Nb solubility in  $\alpha$ -Zr is decreased significantly from 0.6wt% Nb to about 0.2 – 0.3 wt% for materials containing 400-700 ppm Fe and 500-700 ppm O.
- The  $\beta_{Zr}$  deteriorates the Zr-Nb corrosion performance in 360°C out-of-pile water corrosion test, while increased tetragonal ZrO<sub>2</sub> volume fraction and the existence of columnar grains correlated with good corrosion performance<sup>2</sup>. However, it is not clear yet whether these oxide microstructure characteristics are a result of the lower corrosion rate or if the characteristics are really the cause of the good corrosion resistance.

### 4- MECHANICAL PROPERTIES

The mechanical properties of the fuel assembly and the CANDU/RBMK Pressure Tubes are crucial for its satisfactory performance during class I-IV operation as well as during intermediate storage.

Cracking of zirconium alloy fuel assembly components by stress corrosion cracking (SCC) from iodine species or Metal Vapour Embrittlement (MVE) by Cs/Cd can reduce the fracture toughness of Zr alloys to very low values (1-2MPa/m) during PCI incidents. Cures for such processes (e.g. Zr liners, CANLUB coatings) are not perfect and do not prevent the most severe examples that can occur following large power ramps.

Delayed Hydride Cracking (DHC) in Pressure Tubes is a repetitive mode of crack growth, whereby hydride precipitates at small notches (or asperities) and grows until a crack propagates through it. The crack blunts at the end of the hydride and the cycle repeats. Fracture toughnesses of ~7MPa/m are typical of DHC.

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<sup>1</sup> Earlier results by CEA indicate phase transformation temperature of 600°C.

<sup>2</sup> Similar results have been shown by others previously.

Both types of cracking processes have certain limitations; due to chemistry for SCC, and the stress field around the hydride particle for DHC. These limitations have been detailed in order to show where and when these processes cannot occur. For instance, the chemistry of Iodine SCC ensures that cracks cannot grow unless fresh iodine is allowed to react chemically with Zr for ~20 mins. and will again arrest when all the iodine reacts to non-aggressive species (after ~1.5-2 hrs.); DHC cracks will not initiate without long incubation times (~1yr.) if the cracking temperature is not approached from above; MVE cracks require the metal vapour to be able to wet a completely clean (oxygen free) Zr surface. Thus, these limitations have to be considered before jumping to the conclusion that such cracking processes have occurred.

In the year 2003 the highlights were as follows:

- Studies of hydrided nonirradiated Zry-4 in RXA and SRA conditions showed that the ductile-brittle transition in the RXA and SRA materials increase with temperature and is much lower for the former material condition. The difference in mechanical behaviour of the two material conditions at similar hydride concentrations appears to be related to:
  - that the hydrides in the SRA material tends to be thin and oriented in the hoop direction as a result of the SRA elongated grain structure. On the contrary hydrides in RXA material tends to be thicker (and larger in size) and more oriented in the radial direction. Thick, elongated hydrides oriented perpendicular to the stress direction crack first.
  - In-situ observations during deformation indicated that some hydride platelets may undergo plastic deformation up to 80 % at 20°C before fracturing. The majority of the platelets could become deformed by up to 30 %, before cracking.
  - In the same study modeling work suggests that the observed increase in strength when the hydrogen content increases is related to the harder hydride phase reinforcing the softer matrix like in a composite material.
- The most recent data obtained after 6-cycle irradiation in the Kashiwazaki-Kariwa-5 BWR showed that High Fe Zry and High FeNi Zry, which have an increased amount of Fe and/or Ni above the upper limit of Zry-2 chemical specification, had similar ultimate tensile strength, yield strength, ductility and fatigue strength as that of standard Zry-2.
- Irradiation of fuel with MDA, ZIRLO and Zry-4 reference in the Spanish Vandellós II PWR shows that at a fast fluence of about  $11 \cdot 10^{25} \text{ n/m}^2 (E > 1 \text{ MeV})$  the yield strength is similar for the different alloys despite the fact that the chemical composition is significantly different.

## 5-DIMENSIONAL STABILITY

Review of the literature of dimensional stability has found moderate activity in year 2003, as well as in late 2002. Also papers from the Thirteenth International Symposium on Zirconium in the Nuclear Industry (2001) finally became available in published form in 2003. Highlights include:

- Hydrogen in zirconium alloys has been firmly recognized as a significant contributor to dimensional stability. In addition to expansions caused by the larger specific volume of zirconium hydrides as compared to the zirconium matrix, it appears that there may be an influence of hydrides and/or hydrogen on the mechanism of growth and creep.
- The newer PWR alloys and optimized BWR alloys have improved corrosion resistance and, thus, lower hydrogen effects.
- BWR channel bow has been reported to be a concern. The bow mechanism has not yet been defined.
- Irradiation growth of M5 and E635 is low and non-accelerating to equivalent burnups of >65 MWd/kgU.
- Fuel rod, assembly and grid growths of the newer PWR alloys (M5, ZIRLO, Alloy A, MDA) appear to be lower than for previous standard Zircaloy-4.
- Zircaloy-2 with optimized microstructure appears to be adequate for BWRs.
- Pressure tube (Zr2.5Nb,AECL) in-reactor dimensional changes have been correlated to controllable fabrication variables.
- In-reactor creep of Zircaloy has been shown to increase for increases in irradiation temperature, neutron flux, stress, and cold work. The relationships have been quantified for a range of variables relevant to reactor performance. It has also been shown that thermal creep (a non-irradiation effect) contributes to in-reactor creep.
- Zirconium alloy chemistry variables are shown to have effects:
  - increased C increases growth
  - the effect of Sn on creep and growth is still controversial
  - effect of sulfur is strong: an increase from 5 ppm S to 25 ppm S decreases creep significantly
  - in general, Nb additions appear to lower creep and growth

- Empirical understanding of most component dimensional stability issues is good. Areas where more data is required include:
  - detailed temperature dependence of creep and growth in the 300-400°C (573-675K) range
  - possible synergistic effects between hydrogen and growth/creep mechanisms.
  - data out to projected end-of-life burnups
  - factors which affect bow and lean of components (BWR channels, PWR assemblies), including growth, hydrogen and residual stresses.
  - high burnup and high fluence effects on the “constant volume” assumption of irradiation growth.
  - effects of Sn on in-reactor creep and growth
- Fundamental mechanism understanding is still lacking in several areas
  - critical factors affecting formation of c-component dislocations
  - chemistry and microchemistry effects on growth (for example, why are the growth behaviors of M5 and E110 (both basically Zr-1Nb alloys) so different?)
  - the role and relative importance of various point defect sinks in determining creep and growth characteristics

## 6-CORROSION & HYDRIDING

In the absence of a major conference reporting on zirconium alloy corrosion this past year, there has been little progress made in our understanding of Zr corrosion and H uptake mechanisms. Other studies of zirconia ceramics and zirconium have provided useful background information, however, that helps to understand what is happening.

It has been shown that zirconia thermal conductivity decreases significantly with increasing temperature in the range of temperatures expected for the oxide/metal interface temperatures for highly-rated fuel cladding with thick oxide films. This would provide a feedback loop because increasing the metal/oxide interface temperature by decreasing the oxide thermal conductivity will increase the corrosion rate.

In zirconia ceramics with low silica impurity contents (as low as 20ppm) siliceous particles have been observed at grain triple points. This suggests that similar particles could be present in oxide films formed thermally on Zr alloys. The important unknown is generally the extent to which the Si impurity in Zr alloys is present as a Zr silicide intermetallic or is substituted in the other intermetallic phases.



Other studies have shown that it is the vacancy content in stabilised zirconia ceramics that is the primary factor in the stabilisation of the tetragonal or cubic forms of zirconia, and not the presence of the aliovalent additive (Y,Ca,Mg etc.). this provides a further explanation for the high concentrations of tetragonal zirconia present at oxide/metal interfaces, and the early observations of enhanced corrosion by N impurities, since cubic zirconia stabilised by nitrogen is very brittle and fragments easily.

Electrical measurements on oxide films (EIS and other techniques) continue to be reported, but no clear impact on our understanding of corrosion processes has been made.

A few results of corrosion tests have been reported. The most interesting were the results showing the good corrosion resistance of Zr/S binary alloys. A study of binary Zr/Nb alloys in the Nb range 0.05-5wt.% showed two corrosion rate minima. One in the 0.1-0.2% Nb (Ozhennit) region and the other at ~1wt.%Nb provided final anneals were below the monotectoid temperature.

Heavy ion irradiation experiments have become prolific, largely due to a single Chinese group, but have not, so far, contributed to our understanding of irradiation effects on the corrosion of Zr alloys. However, the possibility of improving the corrosion resistance of Zr alloys by implantations of Y ions has been shown. The persistence of such improvements has not yet been established.

Progress on hydrogen uptake mechanisms, and understanding the effects of irradiation on hydrogen solubility has not been significant this year. Thus, we do not know whether irradiation will enhance trapping of H, and whether this will affect DHC. Difficulties with passivation of intermetallics used as hydrogen storage materials, however, suggests that the idea of intermetallics as "windows" for H entry into the metal may be incorrect. Reducing hydrogen uptake in CANDUs by adding oxidising ions (e.g.nitrates) to the coolant has been suggested. Whether this will be a better approach than allowing radiolitic oxygen buildup remains to be seen.

Recent in-reactor corrosion results show 3 cases of fuel defects in BWRs and no corrosion related fuel defects for the PWR side. The reasons of the BWR fuel defects are still not really known.

The performance experience with the cladding materials LK2, LK2+, and LK3 from various BWRs reveals for LK2 and LK2+ a late increased corrosion and hydrogen pickup at  $>30$  MWd/kgU in most reactors. This increase was more pronounced for LK2 than for LK2+ and differs somewhat from reactor to reactor. In the BWR KKB LK2 shows a rather moderate increased corrosion and no increase of hydrogen pickup. In this BWR in an irradiation experiment in 1998 to 2001 the ranking in the corrosion behavior of LK2+ and LK3 was found different than in other BWRs, indicating that water chemistry can play an important role even in the relative ranking of different cladding materials. In KKB the effect of pre-oxidation at  $> 400^{\circ}\text{C}$  in a steam-oxygen gas to about  $2\text{ }\mu\text{m}$  was also found to be different than in other BWRs. Whereas in KKB spalling and thick oxide layer was seen on pre-oxidized LK3 and LK2+ claddings normal corrosion rate was observed in other BWRs with such claddings.

In the Russian reactor type RBMK, a graphite moderated pressure tube reactor with an exit void content similar as in BWRs a very heavy nodular corrosion is observed for the Sn free E110 cladding. E635 shows a much better behavior in this reactor.

Although the behavior of Zry-2 seems to be adequate for future demands in BWRs, development activities of advanced cladding materials are still continuing. Sample irradiations in a Japanese BWR reached exposure times up to 2500 days and a fast fluence of  $1.5\text{E}22\text{ n/cm}^2$ . The tested Zry-2, High-Fe and High-FeNi coupons have a rather low A-parameter ( $4\text{E}-20\text{h}$ ) and show a pronounced late increase of corrosion and hydrogen pick up (HPU) at an exposure time of  $>1500\text{ d}$ . Zry-2 with a somewhat higher A-parameter shows less late increase in corrosion. However HiFi with the same somewhat higher but a higher Fe content than High-Fe reveals the most pronounced late increased corrosion.

As far as the PWR claddings are concerned, most publications deal with the corrosion experience of the advanced Zr-alloys, such as M5, ZIRLO, Duplex ELS, E110, and E635. The present experience with M5 ranges up to a fuel rod burnup of 70 MWd/kgU. The very good corrosion behavior (low oxide thickness and hydrogen pickup) of M5 is due to a low sensitivity to temperature and linear power. Also for ZIRLO the data base on corrosion performance is continuously increasing. However, the corrosion performance of ZIRLO is not much better than that of low-Sn Zircaloy-4, as can be concluded from an irradiation program for four cycles in the Spanish PWR of Vandellós II. Only after the 4<sup>th</sup> cycle, the oxide layer thickness of low tin Zircaloy-4 fuel rods was with 40 to 100 µm noticeable thicker than that of ZIRLO (40-70µm). Some low tin Zry-4 rods developed a hydride rim induced increased corrosion. Since several years the large effect of Sn on the corrosion behavior of ZIRLO was discussed by Westinghouse. An optimized ZIRLO with a Sn content of 0.67% was developed and tested in PWR. The results of lead test irradiations extend now up to about 50 MWd/kgU and show a significant improvement. The corrosion data base with Duplex claddings, applied by Westinghouse-Sweden (former ABB) for their fuel reloads in the German high duty PWRs, extends now up to a burnup of 67 MWd/kgU and is being extended further. The high corrosion resistance agrees with former publications by Siemens. The Russian PWR cladding material E110 exhibits also a very high corrosion resistance under normal PWR conditions. However E110 has high sensitivity against oxygen. Even low O concentrations in the coolant, such as 15 ppb, can result in a strong increase of corrosion. The Sn containing alloy E635 appears to be less sensitive.

## 7-WATER CHEMISTRY EFFECTS

Historically, water chemistry has impacted fuel performance through AOA and/or excessive fuel clad corrosion in most cases in relation to CRUD fuel clad deposition. However, neither AOA nor fuel clad excessive corrosion is only a result of the water chemistry. In both AOA and fuel clad excessive also fuel rod duty is a crucial parameter and in the latter case, also fuel clad microstructure has a major impact on corrosion.

The current trend in both PWRs and BWRs tends to increase the corrosion duty due to more aggressive core loading and higher discharge burnups. Concurrently, the coolant water chemistry is being modified to reduce plant activity build-up and decrease the cracking tendencies in reactor internals. Examples of water chemistry changes for BWRs are: HWC, Zn-injection, Fe-injection, O-injection, NMCA. For PWRs the corresponding changes are: increased maximum LiOH concentration, increased maximum boron coolant concentration (for longer cycles), Zn-injection. To improve the corrosion resistance of the fuel clad materials, the fuel vendors are modifying their current fuel clad product for BWR applications while new materials (ZIRLO and M5) have been developed for PWRs.

In the year 2003, the following key events were noted, see Table below and following bullits.

Table Key corrosion events in the year 2003.

Browns Ferry 2	Cy 12, 2001 - 2003	<ul style="list-style-type: none"> <li>• Implemented NMCA at EOC 11 (3/01).</li> <li>• Zn-injection, 6.5 ppb in RW</li> <li>• Affected fuel is GE13B/P6 claddings that failed in their second cycle. 63 failed assemblies due to excessive corrosion during CY12.</li> <li>• BF-2 changed out their condenser tubes to Ti-tubes 8-10 years ago.</li> </ul>
River Bend	CY 11, 2003, Smith, 2003	<ul style="list-style-type: none"> <li>• Six failed assemblies of first cycle fuel-</li> <li>• Siemens ATRIUM-10 (LTP)</li> <li>• Water chemistry apparently within specification</li> <li>• No NMCA</li> <li>• Zn-injection</li> </ul>

- BWR Noble Metal Chemical Application (NMCA) is still a concern for US utilities and it appears that NMCA with/without Zn-injection tend to increase fuel clad corrosion rate that may result in oxide spallation and in the worst case fuel failures
  - Fuel clad corrosion failures occurred in Browns Ferry 2, CY12 and River Bend, CY11. A total of 63 leaking bundles were found in BF-2 and 6 the corresponding figure was 6 failed assemblies for RB. BF-2 did apply both NMCA and Zn-injection while only Zn-injection was applied in RB.
  - New hot cell PIE of Duane Arnold (first plant to apply NMCA) 3-cycle rods found a Zn-enriched tenacious crud of significant thickness (~50 µm) and surface spallation caused by flaking of the tenacious crud (containing about 30-40 % Zn) and part of zirconium oxide.
  - HNP-2 eddy current lift-off measurements show higher than expected fuel clad oxide thickness on some reloads at EOC16 (1 NM Cycle) and EOC 17 (2 NM Cycles)
- PWR AOA in US is under control by reducing fuel peaking (by reducing max. fuel enrichment) at high temperature plants but current trend to increase enrichments in some plants may result in reoccurrence of AOA
- Elevated constant pH 7.3-7.4 (need Li at 5-6 ppm) chemistry approaches for crud reduction under assessment.

## 8-MANUFACTURING

The development of manufacturing of the zirconium alloys has, during the last years, been characterised by decreased variation in process parameters, to cope with higher demands on the materials; increased efficiency, in order to reduce manufacturing costs; and introduction of new materials, again to comply with higher demands on the cladding.

In all these cases, it is important to be aware of the possible influence of the changes on materials properties not in focus for the change of the process or the new alloy introduced. For instance, a change to improve the corrosion properties by alloying with niobium may change the mechanical properties during power ramp, i.e. that the same PCI rules may not apply.

The main key points are the following:

- The impact of Calendra process route on texture, microstructure hydriding behaviour, residual stress and mechanical anisotropy was investigated in one paper.
- Two studies investigated different methods to join materials. More specifically, the diffusion bonding of stainless steel to Zircaloy-4 in the presence of Ta as an interlayer and electron beam welding between Zircaloy-4 and stainless steel 304L were investigated.
- A processing map using the strain rate sensitivity parameter was developed for Zr–2.5Nb
- A study of practice related to process control and process improvement by statistical methods was presented. The advances in production theory, in monitoring techniques and in the statistical methodology enable the use of new and more efficient procedures which help the implementation of a strategy of continuous quality improvement.

## 9-PRIMARY DEFECTS AND SECONDARY DEGRADATION

Defect free fuel is crucial to maintain a low fuel cycle and maintenance cost.

The following key events occurred during year 2003:

- In US, 10 BWRs have on-going failures:
  - Debris: Brunswick-1 and -2 (GE14B), LS-1 (ATRIUM 9B), and possibly Perry (all 10x10). The 10x10 fuel design seems to be more sensitive to debris fretting failures.
  - Crud-induced: River Bend Cycle 11
  - High elevation cladding corrosion failures in BF-2 and VY. To assess the root cause, 5 rods (3 failed, 2 sound) will be shipped to Vallecitos in 2003 for hot cell examinations in 2003-2004.
  - Suspect PCI in 8x8 fuel: Cooper
  - Zr-Fe liner (0.4wt%Fe in Zr-sponge liner) /manufacturing PCI like failures in three U.S. BWRs: LS-1&2, QC1. A total of 11 failed ATRIUM 9B. The burnups of the failed rods ranges from 12-37 GWd/MTU. Most failures occurred following control rod pulls, but the starting and ending power levels were all within the PCI restriction limits (<8 KW/ft). To identify the root cause six rods will be shipped to Studsvik in 2003 for hot cell examinations.
- BWR channel bow caused slower blade insertion time at several newer BWR4-6s with C lattice core design and abrasion marks on channel surfaces indicate mechanical interferences. Interference occurred in fuel with a certain GNF thick-thin channel design at burnup ~40 GWd/MTU or higher. Root cause is under evaluation
- Grid-rod fretting continues to be the main failure root cause in US PWRs. The 46 FA failed in the year 2002 due to grid-rod fretting are all of the Westinghouse design.
- The new grid spring design of the Westinghouse RFA FA appears to significantly reduce the grid-rod fretting tendency that have been a problem for the older V5H grid spring design.
- The fuel assembly bow has decreased somewhat in EDF plants. The rod drop time, and drag forces have decreased significantly in particularly the 1300 MWe reactors.

- 39 assemblies in the Nogent 2 Plant CY 11 failed event. The plant was shut down 5 months before the scheduled outage. It was reported that no fuel washout had occurred. The primary failure cause was grid to rod fretting at bottom grid in thrice burned F/As.
- The number of degraded BWR liner fuel rods were small
  - 3 rods degraded out of 8 failed Framatome ATRIUM 9B and ATRIUM 10B (both with Fe doped liner)
  - 0 rods degraded out of 6 failed GE14B (liner)
- A favourable fuel pellet microstructure may improve PCI/PCMI performance.
  - In Russia “soft” pellets are being designed for VVER fuel where fuel additives of mullite and niobium oxide (less than 0.5% in total) substantially accelerate fuel creep.
  - Another feature that may result in better PCI/PCMI performance of the fuel developed by others is the existence of glossy phases ( $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ ) in the grain boundaries. These phases will increase the grain boundary sliding and thereby result in higher pellet creep rate under compression (softer pellet).
  - Also fuel microstructures that reduce TFGR during a ramp will improve PCI performance since less TFGR will reduce clad straining. Results presented this year show that larger grains and intragranular SPPs that act as FG bubble pinning sites may reduce TFGR
  - Ramp data shows that 2-cycle  $\text{Cr}_2\text{O}_3$  doped  $\text{UO}_2$  fuel show much better PCI performance compared to that of standard (non-doped)  $\text{UO}_2$  fuel. The  $\text{Cr}_2\text{O}_3$  doped fuel has much larger grains than that of the standard (non-doped)  $\text{UO}_2$  fuel and will increase diffusion distance of the fission gases to fuel rod void volume. The recorded FGR during ramps to 460-468 W/cm were 8 and 16.5% for the  $\text{Cr}_2\text{O}_3$  doped and standard fuel, respectively.
  - Hot cell examinations of ramped  $\text{UO}_2$  fuel with two different burnups and a MOX fuel rod shows that the fuel crack pattern at the pellet periphery is very different. The low burnup  $\text{UO}_2$  rod had significantly less peripheral cracks compared to the high burnup  $\text{UO}_2$  rod and MOX rod. The larger abundance of pellet periphery cracks for the high burnup  $\text{UO}_2$  rod and MOX rod was explained by: 1) its higher fuel temperature during the ramp and 2) larger degree of intragranular FG swelling during the ramp.

## 10-CLADDING PERFORMANCE UNDER ACCIDENT CONDITIONS

The RIA-simulation tests performed in the 90's on high burnup fuel rods showed cladding failures, and fuel dispersal at surprisingly low fuel peak enthalpies. These results triggered efforts in the nuclear industry to review the applicability of the data to high burnup cladding. Nuclear bodies in different countries have expressed concern about the applicability of the existing LOCA and RIA criteria to high burnup LWR fuel. This concern is related to that at high burnups, some new phenomena occur that was not envisioned at the time the current LOCA and RIA criteria were developed. These criteria were based upon results from fuel rods with Zry-2 and -4 claddings that either were non-irradiated or were irradiated to a low burnup level. The high burnup phenomena that may impact LOCA/RIA fuel performance are the development of:

- A porous rim at the peripheral region of the pellet, where the local burnup exceeds the pellet average by a factor of two or more
- A chemical bond between the pellet periphery and the cladding inner surface.
- A high rod internal gas pressure
- Fuel relocation in ballooned area of the fuel rod
- The development of an oxide at the fuel clad outer surface during in-reactor irradiation. The in-reactor fuel clad oxidation will also increase the hydrogen content of the cladding.

The LOCA/RIA fuel performance may also be impacted by the situation today of replacing the Zircaloy (Zry-2 and -4) materials with new Zr-Nb materials such as ZIRLO and M5.

Highlights of the year 2003 are the following:

- RIA tests in NSRR shows that the failure enthalpy decreases with increased clad hydride content. A hydride rim of significant thickness (100  $\mu\text{m}$ ) reducing clad ductility more compared to that of a clad with homogeneously distributed hydrides.

The ductility is further decreased from irradiation hardening of the fuel cladding. Also clad stress state impacts RIA fuel clad performance. The ductility decreases in

the order: uni-axial stresses  $\rightarrow$  biaxial stresses with a stress ratio of  $\frac{\sigma_{\text{tan}}}{\sigma_{\text{axial}}} = 2$  (burst

test)  $\rightarrow$  biaxial stresses with a stress ratio of  $\frac{\sigma_{\text{tan}}}{\sigma_{\text{axial}}} = 1$  (RIA test). During the RIA

test, the large friction between the expanding pellet and the cladding will result in the ratio of  $\frac{\sigma_{\text{tan}}}{\sigma_{\text{axial}}} = 1$ . The implication of these results is that to obtain relevant

results it is crucial that the stress state in a RIA simulation test is similar to that

during a RIA, i.e.  $\frac{\sigma_{\text{tan}}}{\sigma_{\text{axial}}} = 1$ .



Hoop strains measured on-line with strain gages showed that the cladding failure strains were 0.33% and 0.37% during the RIA transients of the FK-10, -12 tests of BWR fuel in NSRR. These values are below the elasticity limit for irradiated material which means that PCMI clad failures occurred without any plastic deformation.

RIA tests of rods with PWR ZIRLO and MDA fuel claddings with burnups of 58-60 MWd/kgU, were performed in the OI-10 and, the OI-11 NSRR tests. The MDA test fuel rod was subjected to a peak fuel enthalpy of 0.44 kJ/g (104 cal/g) and 5.6 msec. pulse-width without failing. The ZIRLO rod with a corresponding pulse width of 4.4 msec. failed at 120 cal/g, but the failure started at the location where the welded thermocouple was attached to the fuel cladding. Thus the failure could be an artefact due to the weld.

In CABRI, ZIRLO and M5 fuel rods with a burnup of about 75 MWd/kgU were tested without failing. The pulse was about 30 msec. in both tests. The ZIRLO rod showed an average oxide thickness of 75 microns, but without evidence of initial spallation and a high mean hydrogen content and hydride concentrations at pellet-pellet interfaces. The ZIRLO fuel rod was subjected to a maximum average fuel enthalpy of 90 cal/g. During the test, the instrumentation recorded a late event which initially could be interpreted as a clad failure. Later, a careful visual inspection of the rod did not reveal any indication of clad failure, but significant spallations. Conclusive information on clad integrity is expected to be obtained by the rod puncturing and subsequent gas analysis that is foreseen in fall 2003. No details was presented on the M5 fuel rod.

RIA tests in the Russian IGR and BGR pulse reactors indicate that no fuel fragmentation occurred and that the fuel cladding (E110) failure threshold level is in excess of 160 cal/g.

- Based upon clad-to-coolant heat transfer tests in the CEA PATRICIA loop the heat transfer correlations were assessed to be able to correctly model the heat transfer conditions during a RIA pulse. These correlations were implemented in the SCANAIR code that was used to model a RIA pulse of a 4-cycle UO<sub>2</sub> rod. The code calculations showed that the fuel enthalpy resulting in *dnb* depends strongly on the zirconia thickness and on the fuel-clad heat-transfer modelling.

In-pile dryout testing of fuel rods in the Halden research reactor indicated that fuel rods can be subjected to severe dry-out with PCTs ranging from 950-1200°C, in the minute scale, without failing. For licensing purposes, one has to assume that dry-out (BWRs) and *dnb* (PWRs) results in fuel rod failure. The Halden results indicate however, that limited dry-out does not result in fuel failures.

The work of the REP Na-1 Task Force shows that the RepNa-1 test is non-representative and therefore should not be included in the development of revised RIA criteria. The current conclusion based on signal analysis is that the REP Na-1 failure occurred between 30-50 cal/g and not at 30 cal/g that was reported earlier.

Work sponsored by EPRI/EDF/RFP have resulted in a revised RIA criteria for core damage and fuel rod failures. The core damage criterion is related to incipient fuel melting. The assumptions for these criteria are that the fuel rods show NO oxide spallation and that the pulse width > 20 msec.

- Russian LOCA integral tests indicate that there is no significant difference in LOCA performance existing between fresh and pre-irradiated fuel up to the burn-up of 50 MWd/kgU

Integral thermal shock tests with irradiated low-Sn Zircaloy-4 PWR fuel rods with a burnup of 48 MWd/ were performed at JAERI. The cladding oxide thickness ranged between 18 to 25µm. The test rods were axially restrained during the quenching phase. One test rod oxidized to about 30%ECR, ruptured during quenching, while two other rods oxidized to about 16 and 18%ECR, respectively, survived the quench.

Argonne National Laboratory LOCA tests of unirradiated Limerick BWR Zry-2 cladding filled with zirconia pellets and internally pressurized show that the ECR value increases as the ballooning circumferential strain increases. The results from the Limerick BWR fuel rod (≈56 GWd/MTU) tests indicate that some fuel particles (<1 g) are blown through the burst opening following burst.

LOCA oxidation and ring compression tests of Zr-Nb alloys shows that:

- The oxidation behaviour and resulting hydride embrittlement of E110 (Russian Zr1Nb alloy) and M5 (French Zr1Nb alloy) is very sensitive to the manufacturing process. Both a decrease in Al+C+N alloy content and maintaining the final annealing temperature lower than the eutectoid temperature, during the late part of manufacturing, improves corrosion resistance and thereby reduces hydrogen pickup.
- The ductile behavior of several experimental variations of E110 cladding is comparable to or in some cases even better than that of standard Zircaloy-4 cladding.
- The ductility of E110 oxidized cladding is very sensitive to surface effects. Cladding etching tends to increase oxidation and hydrogen pickup and making the material brittle. However, belt polishing leads instead to a delay of the onset of nodular oxidation, during the LOCA event, and a reduction of hydrogen pickup and therefore improved clad ductility.

Double-face steam oxidation tests were carried out on fresh M5™ and low-tin Zircaloy-4 and on material pre-hydrided to 200 ppm. The results indicated that the oxidation behaviour of M5 and Zry-4 are similar and that Baker-Just correlation is conservative. The fracture load in room temperature ring compression and impact loading tests was similar for fresh M5™ and Zircaloy-4 samples single-face oxidised to various ECR values.

LOCA Transient Fission Gas Release was studied in out-of-pile annealing tests of irradiated fuel at a burnup of about 48 MWd/kgU.

Information on the first LOCA trial runs and also planned LOCA single pin tests in the Halden research reactor were given. The Halden experiment is very different from other on-going LOCA tests. In the Halden experiment nuclear heating will apply contrary to other out-of-pile tests where the heating is performed from the outside of the fuel. It is planned to use fuel rods irradiated in commercial reactors to burn-up levels exceeding 50 MWd/kg. Also intermediate burnup fuel (lower than 50 MWd/kgU) may be tested.

- The IAEA has initiated a new Coordinate Research Project (CRP) on the improvement of models used for fuel behaviour simulation, FUMEX II (2002-2006). The Project FUMEX II focuses on specific topics linked to extended burn-up, such as thermal performance, fission gas release and pellet to clad interaction, for model development and code validation.

Various code calculations were performed with RELAP5-3D, CASCADE-3D, TRANSURANUS code and TRAC-M codes and reported. A new FRAPCON-3 version is to be issued early 2003 including new/revised fuel (UO<sub>2</sub> and MOX) models.

BNL calculations show that the RIA pulse widths for a BWR Rod-Drop Accident (RDA) is significantly longer than that of PWR Rod-Ejection Accident (REA) or PWR Boron-Dilution Accident

RIA studies performed at ENUSA for a 3 loop PWR core at HZP and EOC conditions indicated that the margin in deposited enthalpy increased significantly when going from 1D axial methodology to 3D best estimate methods. The main sources to the increased margin were the realistic kinetics and power redistribution during the transient.

- Power-oscillation studies indicate that fuel rods may fail not by PCMI (as was thought before) but rather due to LOCA-like oxidation with possible ballooning and rupture as the failure mode. Work is underway to hopefully resolve this issue by 2004.

## **11- FUEL PERFORMANCE CRITERIA AND EXPERIENCE DURING DRY STORAGE**

The permanent spent fuel repository Yucca Mountain (YMP) and the AFR intermediate storage facility at Skull Valley continue to be delayed. The 2010 date for acceptance of fuel at YMP has been put in doubt. The on-site dry storage facilities keep growing in number with 27 currently licensed and 15 about to be licensed.

Significant new fuel related guidance documents for dry cask storage have been and will be issued by the USNRC, that:

- Define subcriticality requirements,
- Modify and clarify burnup credit procedures,
- Modify and clarify the damaged fuel definition,
- Establish fuel integrity criteria for normal storage and consideration of hypothetical transport accident effects on fuel integrity, criticality and retrievability.

The revised regulations establish a 400°C limit on fuel cladding during normal storage and 570°C for short operations such as drying, combined with a 90 MPa stress limit with a yet unclear application. Thermal cycles are also restricted to <10 cycles and for <65°C. This shifts the burden to the maintenance of low decay heat and long spent fuel pool cooling times for the fuel; alternately, the development of higher thermal capacity casks will alleviate this situation.

Cask vendors are able to keep cladding temperatures below 400°C during normal storage with reasonable prior cooling times and the two major cask vendors, when queried, indicated that they can maintain <400°C even during vacuum drying up to certain decay heat and burnup levels.

One vendor has increased the thermal capacity of his casks from about 20 to 40 kW by licensing improved heat transfer calculations and another is in the process of increasing their cask thermal capacity to > 40 kW by modification of the fuel basket design as well as the modeling methods. A second important development is the forced helium drying process for casks by Holtec, which can keep the temperatures below that of vacuum drying levels and reduce the drying time.

The NRC has shifted its focus on fuel related dry cask regulations to the effect of potential transportation accidents to assure that fuel failures during such events do not violate dose limit, criticality and retrievability criteria. Impact and fracture resistance of cladding with and without hydride concentrations are two important properties that need to be known. Establishing these properties and developing failure criteria are the next goals of the NRC and industry in order to have the tools and data available for analyzing the effects of the accidents. The projects to accomplish this are on-going and plan to be completed by the end of 2004 at which time regulations may be established.

The fracture toughness testing of thin walled cladding tubing is one of the difficult issues to be resolved since its geometry does not fit the ASTM definitions for this type of test. Development work on this topic is ongoing, but with no satisfactory conclusions to date.

Hydride reorientation from the circumferential to the radial direction in the cladding reduces the margin to fracture by providing a radial crack path. The temperature and stress limits mentioned above are in large part for the prevention of hydride reorientation. New data generated this year have added some, but not a significant amount of information on this topic during the past year, beyond what was already known.

The performance of fuel during actual dry storage conditions has not been monitored (or at least reported) since the tests previously reported on Surry cladding stored in a Castor container. Verification of calculated models would be important.

Economic analyses of back-end storage costs that include all the pertinent cost elements including the effect of high burnup fuel and the effect of delays in the availability of a permanent repository have not been published. A good analysis of many aspects of the storage costs has recently been made by a Japanese author for Japanese technical and economic conditions. These show the clear advantage of dry casks over pools and some other storage options.

## **12- POTENTIAL BURNUP LIMITATIONS**

The burnup limitations that have actually been reached, but have been or are being extended, are:

- Corrosion of Zry-4 in high power PWRs, extended by improved cladding alloys, but not yet finally eliminated,
- Bowing of PWR fuel assemblies contributed in part by growth of Zry-4, extended by improved guide tube materials, guide tube design changes and reduced assembly holddown forces, but not yet finally eliminated
- Bowing of BWR channels, extended by improved manufacturing processes, and in-core channel management programs,
- RIA and LOCA related burnup licensing limits, in the process of being evaluated by additional experimental data and analyses.

**CONTENTS**

<b>1</b>	<b>INTRODUCTION</b>	<b>1-1</b>
<b>2</b>	<b>UTILITY AND REGULATORY BODY PERSPECTIVES (PETER RUDLING)</b>	<b>2-1</b>
2.1	INTRODUCTION	2-1
2.1.1	Regulatory perspective	2-1
2.1.2	Utility perspective	2-2
2.2	NEW DATA	2-9
2.2.1	Regulatory perspective	2-9
2.2.2	Utility perspective	2-11
2.2.2.1	Japan	2-11
2.2.2.2	France	2-13
2.2.2.3	Belgium	2-13
2.2.2.4	Finland	2-14
2.2.3	Fuel vendor perspective	2-14
2.2.3.1	Russia	2-14
2.2.3.2	Westinghouse	2-15
2.3	SUMMARY	2-17
<b>3</b>	<b>ZIRCONIUM ALLOY SYSTEMS (PETER RUDLING)</b>	<b>3-1</b>
3.1	INTRODUCTION	3-1
3.2	NEW RESULTS	3-3
3.2.1	Zr	3-3
3.2.2	Zircaloy	3-3
3.2.2.1	Residual stresses	3-3
3.2.2.2	Matrix composition and phase transformation	3-4
3.2.2.3	Hydrogen	3-4
3.2.3	Zr-Nb	3-7
3.2.3.1	Residual stresses	3-7
3.2.3.2	Second phase particles	3-7
3.2.3.3	Matrix composition and phase transformation	3-8
3.2.3.4	Hydrogen	3-20
3.2.4	Hydrides	3-20
3.2.5	Effects of irradiation	3-20
3.3	CONCLUSIONS	3-23
<b>4</b>	<b>MECHANICAL PROPERTIES (BRIAN COX AND PETER RUDLING)</b>	<b>4-1</b>
4.1	INTRODUCTION (PETER RUDLING)	4-1
4.1.1	Environmentally Induced Cracking of Zr alloys (Brian Cox)	4-3
4.1.1.1	Stress corrosion cracking (SCC)	4-3
4.1.1.2	Liquid metal (metal vapour) embrittlement (LME)	4-4
4.1.1.3	DHC	4-5
4.1.1.4	PCI	4-11
4.1.1.4.1	Initiation of PCI Cracks	4-16
4.1.1.4.2	Modelling PCI Cracking	4-19
4.1.1.4.3	Cures for PCI	4-20
4.1.1.5	DHC	4-22

4.2	NEW RESULTS	4-29
4.2.1	Experimental materials (Peter Rudling)	4-29
4.2.2	Pressure tubes	4-29
4.2.2.1	DHC (Brian Cox)	4-29
4.2.3	Fuel components (fuel claddings)	4-35
4.2.3.1	Yield strength, ultimate tensile strength, ductility and fatigue (Peter Rudling)	4-35
4.2.3.2	Fracture toughness (Peter Rudling)	4-49
4.3	SUMMARY AND HIGHLIGHTS-YEAR 2003	4-49
<b>5</b>	<b>DIMENSIONAL STABILITY (RON ADAMSON)</b>	<b>5-1</b>
5.1	BACKGROUND	5-1
5.2	EFFECTS OF HYDROGEN	5-3
5.3	CHANNEL BOW	5-9
5.4	MATERIAL SPECIMEN GROWTH	5-10
5.5	PWR FUEL ASSEMBLY AND GRID GROWTH	5-11
5.6	FUEL ROD GROWTH	5-13
5.7	CREEP	5-17
5.7.1	Cladding Creep Down	5-17
5.7.2	Pressure Tube Creep	5-21
5.7.3	Creep in Test Reactors	5-25
5.8	PARAMETER EFFECTS	5-28
5.8.1	Effect of Carbon (C)	5-28
5.8.2	Effect of Tin (Sn)	5-29
5.8.3	Effect of Sulfur (S)	5-32
5.8.4	Effect of Niobium (Nb)	5-33
5.9	SUMMARY	5-35
<b>6</b>	<b>CORROSION AND HYDROGEN UPTAKE</b>	<b>6-1</b>
6.1	OUT-REACTOR EXPERIMENTATION (BRIAN COX)	6-1
6.1.1	Oxide Properties	6-3
6.1.2	Oxidation Film Properties	6-12
6.1.3	Corrosion Tests	6-20
6.1.4	Irradiation Effects	6-31
6.1.5	Hydrogen Uptake	6-36
6.2	IN-REACTOR CORROSION RESULTS (F. GARZAROLLI)	6-48
6.2.1	Coolant related in reactor failures	6-49
6.2.2	Corrosion examinations after exposure in BWRs	6-51
6.2.3	Corrosion examinations after exposure in PWRs	6-59
6.3	SUMMARY	6-66
<b>7</b>	<b>WATER CHEMISTRY IMPACT ON FUEL PERFORMANCE (PETER RUDLING)</b>	<b>7-1</b>
7.1	NEW RESULTS PRESENTED IN THE YEAR 2003	7-4
7.1.1	PWRs	7-4
7.1.1.1	Zn-injection	7-4
7.1.1.2	Increased LiOH/pH	7-5
7.1.1.3	AOA/DCP	7-5

7.1.2	BWRs	7-8
7.1.2.1	NMCA with/without Zn-injection	7-8
7.1.2.2	Hatch 1 and 2	7-9
7.1.2.3	River Bend CY11 corrosion failures	7-10
7.1.2.4	Brown Ferry 2, CY12 corrosion failures	7-13
7.2	SUMMARY AND HIGHLIGHTS-YEAR 2003	7-15
<b>8</b>	<b>ZIRCONIUM ALLOY MANUFACTURING (PETER RUDLING)</b>	<b>8-1</b>
8.1	INTRODUCTION	8-1
8.2	NEW RESULTS	8-1
8.2.1	Calandria tubes	8-1
8.2.2	Material joining	8-6
8.2.3	Pressure tubes	8-7
8.2.4	QA/QC	8-7
8.2.5	Zircaloy	8-8
8.2.5.1	Plate/strip	8-8
8.2.6	Zr-Nb	8-8
8.3	CONCLUSIONS	8-9
<b>9</b>	<b>PRIMARY FAILURE AND SECONDARY DEGRADATION (PETER RUDLING)</b>	<b>9-1</b>
9.1	INTRODUCTION	9-1
9.1.1	Primary Failures	9-1
9.1.2	Secondary Degradation	9-9
9.2	RESULTS PRESENTED IN YEAR 2003	9-15
9.2.1	Fuel Performance in failed fuel	9-15
9.2.2	Primary fuel failures	9-15
9.2.2.1	Handling damage	9-17
9.2.2.1.1	Penly 2	9-17
9.2.2.1.2	Palo Verde 1	9-18
9.2.2.2	Manufacturing defects	9-19
9.2.2.2.1	Axial Offset Deviation	9-19
9.2.2.2.2	Weld defects	9-19
9.2.2.3	Fuel Assembly Bowing	9-21
9.2.2.3.1	EDF plants	9-21
9.2.2.3.2	Wolf Creek	9-23
9.2.2.4	CRUD induced corrosion acceleration, oxide spallation and fuel failures	9-24
9.2.2.5	Grid-to-rod fretting	9-24
9.2.2.5.1	Crystal River 3	9-24
9.2.2.5.2	Watford, ANO-1 and -2	9-24
9.2.2.5.3	North Anna 1 and 2	9-25
9.2.2.5.4	Wolf Creek	9-26
9.2.2.5.5	RBMK reactors	9-27
9.2.2.5.6	Nogent 2	9-28
9.2.2.5.7	Out-of-pile tests	9-33
9.2.2.6	Debris Fretting	9-36
9.2.2.7	Fretting due to baffle jetting	9-38
9.2.2.8	PCI and PCMI	9-39
9.2.2.8.1	PCI failures in commercial reactors	9-39
9.2.2.8.1.1	LaSalle 2	9-39
9.2.2.8.1.2	Quad Cities 1	9-49



9.2.2.8.2	Ramp Results	9-52
9.2.2.8.2.1	BWR fuel	9-52
9.2.2.8.2.2	PWR fuel	9-52
9.2.2.8.3	Fuel properties related to PCI/PCMI	9-57
9.2.3	Degradation	9-68
9.3	SUMMARY AND HIGHLIGHTS-YEAR 2003	9-69
<b>10</b>	<b>CLADDING PERFORMANCE UNDER ACCIDENT CONDITIONS (PETER RUDLING)</b>	<b>10-1</b>
10.1	INTRODUCTION	10-1
10.1.1	LOCA	10-1
10.1.2	ATWS	10-5
10.1.3	RIA	10-5
10.1.4	Computer codes	10-11
10.1.5	Current Design Basis Accident issues	10-13
10.2	ON-GOING PROGRAMS	10-14
10.3	NEW RESULTS	10-17
10.3.1	Anticipated Transient Without Scram, ATWS	10-17
10.3.2	RIA	10-17
10.3.2.1	Separate effect tests	10-17
10.3.2.1.1	Materials	10-17
10.3.2.2	Integral tests	10-27
10.3.2.3	Modeling	10-42
10.3.3	LOCA	10-57
10.3.3.1	Separate effect tests	10-59
10.3.3.1.1	Russian results	10-59
10.3.3.1.2	Japanese results	10-66
10.3.3.1.3	French results	10-66
10.3.3.1.4	US results	10-71
10.3.3.2	Integral tests	10-74
10.3.3.3	Modeling	10-87
10.4	SUMMARY AND HIGHLIGHTS – YEAR 2003	10-90
<b>11</b>	<b>SPENT FUEL PERFORMANCE CRITERIA DURING INTERMEDIATE STORAGE AND TRANSPORTATION</b>	<b>11-1</b>
11.1	INTRODUCTION	11-1
11.2	STATUS OF FUEL RELATED REGULATORY REQUIREMENTS	11-4
11.2.1	Introduction	11-4
11.2.2	ISG 19 and 10 CFR 71.55 Subcriticality Requirements During Accidents	11-5
11.2.3	ISG 8, Rev. 2 Burnup Credit	11-7
11.2.4	ISG 1, Rev. 1, Damaged Fuel	11-10
11.2.5	ISG 11, Rev. 3 (to be published) Cladding Considerations for the Transportation and Storage of Spent Fuel	11-12
11.3	EFFECT OF TEMPERATURE AND STRESS LIMITS	11-14
11.3.1	Initial Cladding Temperature and Stresses	11-14
11.3.2	Hydride Reorientation	11-20
11.4	CREEP DATA	11-27
11.5	TRANSPORTATION AND HANDLING ACCIDENTS	11-36
11.5.1	Design Base Accidents	11-36
11.5.2	Accident Analyses	11-37

11.6	UPDATE ON STORAGE CASK DESIGNS AND LICENSING STATUS	11-44
11.6.1	Introduction	11-44
11.6.2	Design and Process Modifications to Meet Temperature Limits	11-46
11.6.3	Drying Operations	11-52
11.6.4	Economics	11-52
11.6.5	Fuel Performance During Dry Cask Storage	11-56
11.7	CONCLUSIONS	11-56
<b>12</b>	<b>POTENTIAL BURNUP LIMITATIONS</b>	<b>12-1</b>
12.1	INTRODUCTION	12-1
12.2	CORROSION AND MECHANICAL PROPERTIES RELATED TO OXIDE THICKNESS AND H PICKUP	12-2
12.3	DIMENSIONAL STABILITY	12-3
12.4	PCI IN BWRS AND PWRS	12-4
12.5	LOCA	12-5
12.6	RIA	12-5
12.7	5% ENRICHMENT LIMITS IN FABRICATION PLANTS, TRANSPORT AND REACTOR SITES	12-5
12.8	DRY STORAGE	12-6
<b>13</b>	<b>REFERENCES</b>	<b>13-1</b>

## 1 INTRODUCTION

The objective of the Annual Review of Zirconium Alloy Technology (ZIRAT) is to review and evaluate the latest developments in zirconium alloy technology as they apply to nuclear fuel design and performance.

The objective is met through a review and evaluation of the most recent data on zirconium alloys and to identify the most important new information and discuss its significance in relation to fuel performance now and in the future. Included in the review are topics on materials research and development, fabrication, component design, and in-reactor performance.

- Within the ZIRAT-8 Program, the following technical meetings were covered:
- Top Fuel 2003, Würzburg, Germany, March 2003
- Jahrestagung, Berlin, Germany, May 2003
- 33rd International Utility Nuclear Fuel Performance Conference, San Diego, CA, June 2003
- 11th Int. Conf. On Environmental Degradation of Materials in Nuclear Power Systems, Stevens, WA, August 2003
- IAEA Seminar on PCMI in Water Reactor Fuels, Brussels, Oct. 2003,
- NRC 2003 Nuclear Safety Research Conference, Washington DC, Oct. 2003

The extensive, continuous flow of journal publications is being monitored by several literature searches of world-wide publications and the important papers are summarised and critically evaluated. This includes the following journals:

- Journal of Nuclear Materials,
- Nuclear Engineering and Design,
- Kerntechnik
- Metallurgical and Materials Transactions A
- Journal of Alloys and Compounds
- Canadian Metallurgical Quarterly
- Journal de Physique IV
- Journal of Nuclear Science and Technology
- Nuclear Science & Engineering
- Nuclear Technology

The primary issues addressed in the review and this report are zirconium alloy research and development, fabrication, component design, ex- and in-reactor performance including:

- Regulatory bodies and utility perspectives related to fuel performance issues, fuel vendor developments of new fuel design to meet the fuel performance issues
- Fabrication and quality control of zirconium manufacturing, zirconium alloy systems
- Mechanical properties and their test methods (that are not covered in any other section in the report)
- Dimensional stability (growth and creep)
- Primary coolant chemistry and its effect on zirconium alloy component performance
- Corrosion and hydriding mechanisms and performance of commercial alloys
- Cladding primary failures
- Post-failure degradation of failed fuel
- Cladding performance in postulated accidents (LOCA, RIA)
- Dry storage
- Potential burnup limitations
- Current uncertainties and issues needing solution are identified throughout the report.

Background data from prior periods have been included wherever needed. Most data are from non-proprietary sources; however, their compilation, evaluations, and conclusions in the report are proprietary to ANT International and ZIRAT members as noted on the title page.

The information within the ZIRAT-8 Program is either retrieved from the open literature or from proprietary information that ANT International has received the OK from the respective organisation to provide this information within the ZIRAT-program.

The authors of the report are Dr. Ron Adamson, Brian Cox, Professor Emeritus, University of Toronto; Al Strasser, President of Aquarius; Dr. Gunnar Wikmark, President of ANT and, Peter Rudling, President of ANT International.

The work reported herein will be presented in three Seminars: one in Lisbon on January 13-15, 2004 and one in Key Largo, Florida, on January 27-29, 2004 and one in Japan on March 29, 2004.

The Term of ZIRAT-8 starts February 1, 2003 and ends January 31, 2004.

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## **2 UTILITY AND REGULATORY BODY PERSPECTIVES (PETER RUDLING)**

### **2.1 INTRODUCTION**

#### **2.1.1 Regulatory perspective**

The objective of nuclear reactor safety is to ensure that the operation of commercial nuclear power plants does not contribute significantly to individual as well as societal health risks, Nuclear Fuel Safety Criteria Technical Review, 2001. Reactor safety is thus primarily concerned with the prevention of radiation-related damage to the public from the operation of commercial nuclear reactors. Safety limits are introduced to avoid fuel failures during normal operation, or to mitigate the consequences of reactor accidents in which substantial damage is done to the reactor core.

In most countries the dose rate limits are defined for a possible off-site radiological release following a reactor accident. Fuel safety criteria that relate to fuel damage are then specified to ensure that these limits are not exceeded. Numerous criteria related to fuel damage are used in safety analyses. These criteria, however, may differ from country to country. Some criteria are used to minimise cladding degradation during normal operation and some are used to maintain cladding integrity during anticipated transients, thus avoiding fission product release. Others are used to limit fuel damage and ensure core coolability during design-basis accidents, or to limit the public risk from low probability severe accidents.

The fuel issues that concerns the regulatory bodies today during normal operation (class I) and anticipated operational occurrences (class II) are:

- oxidation levels higher than predicted,
- excessive internal gas pressure in burnable poison rods,
- incomplete control rod insertion (IRI) events,
- large axial offsets or axial offset anomalies (AOA),
- fuel failures due to high fuel duty,
- adverse effects of water chemistry,
- high crud buildup, and
- accelerated growth of rods and assemblies.

Also performance of high burnup fuel is a concern since the current LOCA and RIA limits are based upon non-irradiated fuel or fuel with very low burnup. In addition, the current criteria were based upon tests on Zircaloy while today other materials are used such as ZIRLO and M5, that may show different material behaviour during such accident conditions compared to that of Zircaloy.

### 2.1.2 Utility perspective

The fuel discharge burnup has increased steadily over time, Figure 2-1 and Figure 2-2. Figure 2-3 shows that also cycle length and enrichment level in US have increased over time.

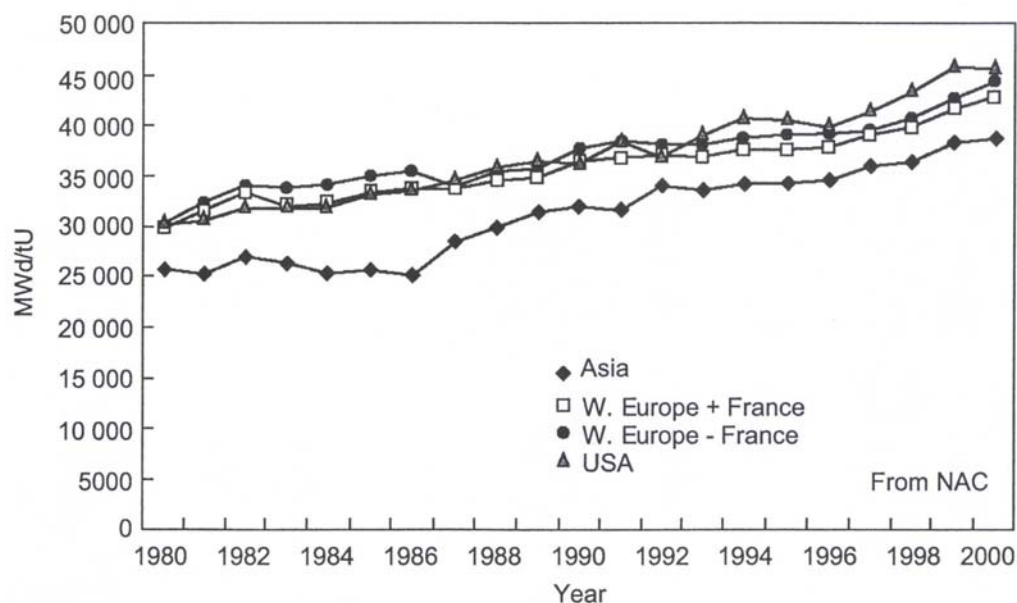
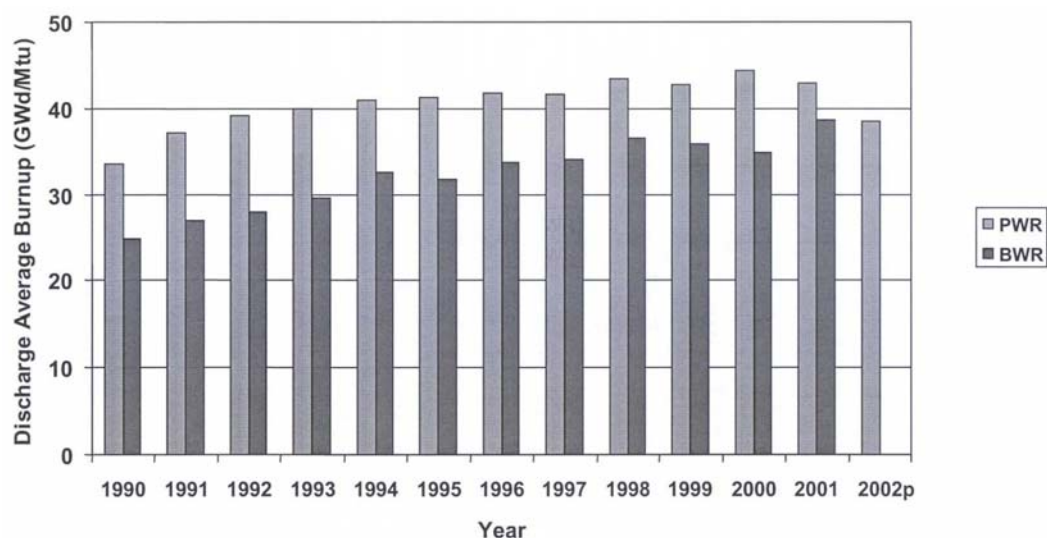


Figure 2-1: Historical Trend of Burnup, Estève, et al., 2002.



c) Trends In Discharge Batch Average Burnup - U.S.

Figure 2-2: High Burnup History in the US, Yang, 2003(b).

### 3 ZIRCONIUM ALLOY SYSTEMS (PETER RUDLING)

#### 3.1 INTRODUCTION

The material performance in-reactor is a function of the reactor environment as well as the material microstructure. The microstructure depends on the chemical composition and the manufacturing process of the alloy. Characterisation of the material microstructure in relation to the material performance can elucidate the mechanisms behind the material performance. This knowledge can be used by fuel vendors to modify the manufacturing process to get optimum material performance in-reactor. Table 3-1 provides a summary of commercial and experimental alloys.

Table 3-1: Zirconium base material currently used.

Alloy	Sn %	Nb %	Fe %	Cr %	Ni %	O %	Others alloy elem.	%	Ref.
<u>1. Commercial alloys</u>									
Zircaloy-2	1.2-1.7	-	0.07-0.2	0.05-0.15	0.03-0.08	0.1-0.14	-	-	1)
Zircaloy-4	1.2-1.7	-	0.18-0.24	0.07-0.13	-	0.1-0.14	-	-	1)
E-110	-	0.9-1.1	0.014	<0.003	0.0035	0.05-0.07	-	-	2)
Alloy E125	-	2.5	-	-	-	0.06	-	-	3)
Zr2.5Nb	-	2.4-2.8	<0.15	-	-	0.09-0.13	-	-	1)
ZIRLO	1	1	0.1	-	-	-	-	-	4)
DX-ELS-Liner	0.5/0.8	-	0.3/0.5	0.2	-	0.12	-	-	5)
PCA-2b	1.3	-	0.3	0.2	-	-	-	-	5)
M5	-	0.8-1.2	0.015-0.06	-	-	0.09-0.12	-	-	6)
<u>2. Experimental alloys</u>									
Zircaloy-1	-	2.5	-	-	-	-	-	-	7)
Zircaloy-3A	0.25	-	0.25	-	-	-	-	-	7)
Zircaloy-3B	0.5	-	0.4	-	-	-	-	-	7)
Zircaloy-3C	0.5	-	0.2	-	0.2	-	-	-	7)
Zr1Sn0.5Fe	1	-	0.5	-	-	0.1	-	-	8)
ZrSnFe	1.3-1.5	-	0.26-0.3	<0.05	-	-	-	-	9)
M4	0.5	-	0.6	-	-	0.12	V	0.3	10)
D2	0.5	-	0.4	-	-	0.1	-	-	11)
High Fe Zry-2	1.5	-	0.26	0.10	0.05	-	-	-	12)
HighFeNi Zry-2	1.4	-	0.26	0.10	0.10	-	-	-	12)
HIFI	1.5	-	0.4	0.10	0.08	-	-	-	17)

Table 3-1: Zirconium base material currently used, Adamson, et al., 2002. Cont'd.

Alloy	Sn %	Nb %	Fe %	Cr %	Ni %	O %	Others alloy elem.	%	Ref.
<u>2. Experimental alloys, Cont'd</u>									
ZrSnFeO	0.5	-	0.4	-	-	0.22	-		13)
Alloy-C	0.4	-	0.5	0.24	-	0.18	-		13)
HPA-4	0.4-0.6	-	Fe	-	-		V		14)
Valloy	-	-	0.15	1.2	-	-	-		7)
Zr.7Fe0.7Ni	-	-	0.7	-	0.7	0.03	-		8)
Zr0.25Fe0.2V	-	-	0.25	-	-		-		7)
E635	1.1-1.4	0.9-1.1	0.3-0.5	-	-	0.05-0.07	-		3)
Alloy-A	0.5	0.3	0.35	0.25	-	0.15	-		13)
Alloy-E	0.7	0.4	0.45	0.24	-	0.13	-		13)
NSF 0.2	1	1	0.2	-	-	0.1	-		7)
T18/I18	1	0.6	0.2	-	0.05		-		15)
NSF 0.5	1	1	0.5	-	-	0.1			15)
Zr3Nb1Sn	1	2-3	-	-	-		-		9)
Ozhenite 0.5	0.2	0.1	0.1	-	0.1		-		7)
M3	0.5	0.5	0.25	-	-	0.12	-		10)
0.2 Nb Zry-2	1.5	0.2	0.15	0.10	0.06		-		15)
0.5 Nb Zry-2	1.5	0.5	0.15	01	0.05		-		12)
D3	1.4	1	0.2	0.1	-		-		11)
EXCEL	3.5	0.8	-	-	-		Mo	0.8	7)
XXL	1.2	0.3	-	-	-		Mo	0.3	12)
T12-15/I12-15	1	1-2	-	-	-		Mo	0.2-0.5	15)
T19/I19	1.4	0.4	-	-	-		Te	0.2	15)
T20/I20	1.2	-	-	-	-		Te	0.6	15)
BAG	-	0.5	-	-	-		Bi	1	12)
T68	0.8	-	0.3	0.1	0.1		Cu/Ta	0.2/0.2	16)
T40	1	-	0.25	0.1	-		Cu/Ta	0.1/0.2	16)
MDA	0.8	0.5	0.2	0.1	-				18)
NDA	1	0.1	0.27	0.16	0.01				19)

- <sup>1)</sup> ASTM; <sup>2)</sup> Shebalov, et al., 2000; <sup>3)</sup> Solonin, et al., 1999; <sup>4)</sup> Comstock, et al., 1996; <sup>5)</sup> Garzarolli, 2001;  
<sup>6)</sup> Mardon, et. al., 2000; <sup>7)</sup> Cox, et al., 1998; <sup>8)</sup> Amaev, 1971; <sup>9)</sup> Garzarolli, et al., 2001; <sup>10)</sup> Mardon, et. al., 1994(b);  
<sup>11)</sup> Besch, et al., 1996; <sup>12)</sup> Ishimoto, et. al., 2000; <sup>13)</sup> Garde, et al., 2001; <sup>14)</sup> Seibold, 2001; <sup>15)</sup> Etoh, et al., 1996;  
<sup>16)</sup> Takeda and Anada, 2001, 17) Ishimoto et al., 2003, 18) Tsukada et al., 2003, 19) Tsukuda et al., 2003.



### 3.2 NEW RESULTS

*In the following the new results presented during the late part of year 2002 up to the late part of the year 2003 are summarized.*

#### 3.2.1 Zr

Charquet, 2002 showed that the sulfur in Zr-S in amounts up to 850 ppm was beneficial for the steam corrosion resistance at 400 °C, see also Section 6.1.3. *Out-of-pile corrosion tests are however not very reliable to predict in-pile corrosion performance and therefore one has to be cautious when interpreting the implications of these results for in-pile corrosion predictions.*

The diffusion behaviour of Al and Zr was investigated in the  $\beta$ -Zr(Al) phase in the temperature range 1203–1323 K by employing single-phase diffusion couples of pure Zr/Zr–2.8 wt% Al, A. Laik, et al., 2002. The interdiffusion coefficients showed a small increase with increase in Al concentration that followed a quadratic compositional relation. Also, the temperature dependence of the interdiffusion coefficients at various compositions was established. The activation energy for the interdiffusion coefficient decreased linearly with an increase in Al concentration and the intrinsic diffusivity of Zr was found to be higher than that of Al in this phase field. The impurity diffusion coefficient of Al in  $\beta$ -Zr was determined by extrapolation of interdiffusion coefficients to limiting concentration of Al and its temperature dependence was provided. A correlation between the impurity diffusion coefficients of various impurities in  $\beta$ -Zr and the atomic radii of the impurity atoms was also supplied in the paper.

#### 3.2.2 Zircaloy

##### 3.2.2.1 Residual stresses

The residual intergranular strains in textured Zircaloy-2 plate samples induced by cooling from 823 K to ambient temperatures, by cold-rolling by 1.5% and 25% and by deforming in tension by 1.5% were measured by neutron diffraction, Holden, et al., 2002. The strong rolling texture, which resulted in two ideal orientations, permitted the interpretation of much of the data in terms of strain tensors for the two orientations. The experimental results were compared with calculations based on the elasto-plastic self-consistent model with no adjustable parameters. Close agreement was obtained for samples in the as-cooled state and deformation in tension by 1.5% while the agreement was less satisfactory for cold-rolling condition.

## 4 MECHANICAL PROPERTIES (BRIAN COX AND PETER RUDLING)

### 4.1 INTRODUCTION (PETER RUDLING)

The mechanical properties of essentially two different components are treated in this section. Firstly, it is the *LWR* fuel assembly and, secondly, it is *Pressure tubes*, e.g., in *CANDU* reactors. The difference between these two components is that the fuel is reloaded after some time in-reactor while the *Pressure tube* is a part of the reactor design and must consequently performance satisfactory during the lifetime of the reactor.

Delayed hydride cracking, DHC, is a failure mechanism that may limit the lifetime of *CANDU* and RBMK pressure tubes, and this mechanism is therefore treated in the pressure tube section. Delayed Hydride Cracking, DHC, is a fracture mechanism that may result in pressure tube failures as well as degradation of failed *LWR* fuel. A better understanding of the relation of the DHC mechanism to the material properties may e.g. assist the fuel vendors to develop products with enhanced resistance towards DHC.

In a *CANDU* reactor the cold-worked Zr-2.5Nb pressure tubes operate at temperatures between about 250 and 310°C, and at coolant pressures of about 10 MPa corresponding to hoop stresses of about 130 MPa. The maximum flux of fast neutrons from the fuel is about  $4 \cdot 10^{17} \text{ n m}^{-2} \text{ s}^{-1}$ .

The pressure tubes used in a *CANDU* reactor are made from Zr-2.5Nb. The tubes are extruded at 815°C, cold worked 27%, and stress relieved at 400°C for 24 hours, resulting in a structure consisting of elongated grains of hexagonal-close-packed (hcp)  $\alpha$ -Zr, partially surrounded by a thin network of filaments of body-centred-cubic  $\beta$ -Zr. These  $\beta$ -Zr filaments are metastable and initially contain about 20% Nb. The stress-relief treatment results in partial decomposition of the  $\beta$ -Zr filaments with the formation of hexagonal-close-packed  $\omega$ -phase particles that are low in Nb, surrounded by an Nb-enriched  $\beta$ -Zr matrix. The hcp  $\alpha$ -Zr grains are oriented with their unique c-axes aligned in the radial-transverse plane, mostly tilted towards the transverse direction.

The mechanical properties of the *LWR* fuel assembly is crucial for its satisfactory performance in-reactor. *Standard Review Plan, SRP*, section 4.2, lists different mechanical failure modes of the *LWR* fuel components and also the corresponding design criterion to ensure that the fuel assembly behaviour is satisfactory. These design criteria are set to ensure that:

- the fuel assembly will not *fail* during normal operation (class I) and anticipated operational occurrences (class II). *Failing* in this sense has a broader meaning, namely that the fuel rod may not be breached and that the dimensional changes of the assembly during irradiation must be limited. The latter requirement is to ensure that control rods can be inserted and that the fuel can be handled during shutdown. Also the BWR fuel outer channel cross section must not have increased to such an extent that it is impossible to pass it through the upper core grid during reloading.

- the fuel remains coolable during an accident (class III and IV). Class IV design basis accident are *LOCA*, *RIA* and earthquake. During class III and IV situations limited fuel failures are however accepted. Another criterion that must be fulfilled in these situations is that it should be possible to insert the control rods.
- During class I and II operation, the following mechanical *failure* mechanisms and corresponding design criterion for the fuel assembly, including its components, are listed in *SRP* section 4.2:
  - Plastic deformation – the component is regarded as *failed* if it is plastically deformed and the appropriate criterion is that the stresses must be lower than the yield stress. *SRP* section 4.2 also state what type of methodology should be used when calculating these stresses. In these calculations the stress in the assembly location subjected to maximum stresses is calculated. In calculating this stress, all types of stresses are taking into account, such as welding residual stress, thermal stress, stress imposed by rod-system differential pressure, etc. It is interesting to note that the criterion on maximum allowable oxide thickness on fuel rods is related to this criterion. If the oxide thickness becomes too large in a *PWR*, the oxide thickness will increase the cladding temperature due to its lower thermal conductivity and would then increase corrosion rate. The oxide thickness would increase further, raising the clad temperature and corrosion rate, resulting in thermal feedback. Since increasing temperature decreases the yield strength of the material, the material would eventually mechanical fail, i.e. plastically deform, provided that the cladding stresses are large enough.
  - Excessive creep deformation that could either result in creep fracture or too large plastic deformations that could e.g. lead to *dryout* due to excessive outward creep of the fuel cladding diameter that would limit coolant flow. Creep occurs at a stress level lower than the yield stress. The corresponding criterion is very general and just specify that the creep deformation must be limited.
  - Fatigue failure – Most fuel assembly components are subjected to fatigue stresses and *SRP* section 4.2 provides the maximum allowable fatigue stress level.
  - *PCI* – The criterion to eliminate this type of failure is by limiting the elastic and uniform plastic deformation in the cladding circumference during a class I and II transient to 1%. This value is of course not sufficiently to ensure that *PCI* failures do not occur. However, the fuel vendors are still designing their fuel so this 1 % limit is achieved in their design.
  - Hydride embrittlement – The criterion just mentions that the hydrogen content in the material must be limited so the fuel assembly component will not fail.

During accident conditions such as *LOCA* and *RIA*, the mechanical performance of the fuel cladding is crucial to meet the objective that the fuel must remain coolable during these types of accidents. In both situations, it is important that the fuel cladding may not fail in a brittle fashion during the *reflooding*<sup>5</sup> phase during *LOCA* and due to *PCMI*<sup>6</sup> during a *RIA* transient.

Fuel vendors have developed codes to model the fuel assembly mechanical performance during class I, II, III and IV situations. To be able to do the modeling correctly, data on mechanical performance of the fuel assembly must exist. The data are generated in two types of tests, either separate effect tests and integral tests. The former test studies only the impact of one parameter at a time on the mechanical performance, see e.g. Adamson and Rudling, 2001. This could e.g., be the impact of hydrogen content on ductility. The data from these separate effect tests are then used by the fuel vendor to develop adequate models in their fuel performance codes. To then verify that the code comes up with the correct prediction on fuel assembly mechanical performance e.g. during a *LOCA*, the code predictions are benchmarked towards integral tests. In the integral test, the fuel assembly design and environment is as similar as possible as is existing in the situation that is simulated in the test, e.g. a *LOCA*.

#### **4.1.1 Environmentally Induced Cracking of Zr alloys (Brian Cox)**

Environmentally induced cracking processes have the potential to materially reduce the strength of reactor components. There are three basically different types of these processes:

##### *4.1.1.1 Stress corrosion cracking (SCC)*

This is probably the best known, and commonest, of these processes as it has been the cause of extensive stainless steel recirculation pipe cracking and cracking of core internals in BWRs, and of Inconel 600 cracking in PWRs. In aqueous solutions the mechanism of cracking is primarily a localised anodic dissolution of sensitised grain boundaries. This sensitization can be caused either by the fabrication route and chemistry of (e.g.) the stainless steel (unstabilised and sensitised stainless steels) or to an irradiation induced sensitization caused by migration of sensitising species to and from the grain boundaries.

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<sup>5</sup> This is the last phase during a *LOCA* situation when the core is reflooded with water that cools the fuel cladding surface imposing very large thermal stresses that may fracture the fuel cladding.

<sup>6</sup> Pellet Cladding Mechanical Interaction, i.e., interaction without the influence of iodine (that would instead result in PCI (Pellet Cladding Interaction)).

## 5 DIMENSIONAL STABILITY (RON ADAMSON)

### 5.1 BACKGROUND

One of the most unique aspects of material behavior in a nuclear power plant is the effect of radiation (mainly neutrons) on the dimensional stability of the reactor components. In fast breeder reactors the Fe and Ni-based alloys creep and swell, that is, they change dimensions in response to a stress and change their volume in response to radiation damage. In light water reactors, zirconium alloy structural components creep, do not swell, but do change their dimensions through the approximately constant volume process called irradiation growth. Radiation effects are not unexpected since during the lifetime of a typical component every atom is displaced from its normal lattice position at least 20 times! With the possible exception of elastic properties like Young's Modulus, the properties needed for reliable fuel assembly performance are affected by irradiation. A straightforward summary of such effects is given by Adamson, 2000, and the ZIRAT Special Topical Report on Mechanical Properties, Adamson and Rudling, 2001.

Practical effects of dimensional instabilities are well known and it is a rare technical conference in the reactor performance field that does not include discussions on the topic. Because of the difference in pressure inside and outside the fuel rod, cladding creeps down on the fuel early in life, and then creeps out again later in life as the fuel begins to swell. A major issue is to have creep strength sufficient to resist outward movement of the cladding if fission gas pressure becomes high at high burnups. PWR guide tubes can creep downward or laterally due to forces imposed by fuel assembly hold down forces or cross flow hydraulic forces – both leading to assembly bow which can interfere with smooth control rod motion. BWR channels can creep out or bulge in response to differential water pressures across the channel wall, again leading toward control blade interference. Fuel rods, water rods or boxes, guide tubes, and tie rods can lengthen, possibly leading to bowing problems. (For calibration, a recrystallized (RX) Zircaloy water rod or guide tube could lengthen due to irradiation growth more than 2 cm. during service; a cold worked/stress relieved (SRA) component could lengthen more than 6 cm.) Even RX spacer/grids could widen enough due to irradiation growth (if texture or heat treatment was not optimized) to cause uncomfortable interference with the channel.

In addition, corrosion leading to hydrogen absorption in Zircaloy can contribute to component dimensional instability due, at least in part, to the fact that the volume of zirconium hydride is about 16% larger than zirconium.

The above discussion leads to the concept that understanding the mechanisms of dimensional instability in the aggressive environment of the nuclear core is important for more than just academic reasons. Reliability of materials and structure performance can depend on such understanding.

A comprehensive review of dimensional stability has been given in the ZIRAT 7 Special Topical Report, Adamson and Rudling, 2002. The sources of dimensional changes of reactor components (in addition to changes caused by conventional thermal expansion and contraction) are: irradiation growth, irradiation creep, thermal creep, stress relaxation (which is a combination of thermal and irradiation creep), and hydrogen and hydride formation.

Irradiation effects are primarily related to the flow of irradiation-produced point defects to sinks such as grain boundaries, deformation-produced dislocations, irradiation-produced dislocation loops, and alloying and impurity element complexes. In zirconium alloys, crystallographic and diffusional anisotropy are key elements in producing dimensional changes.

In the past, hydrogen effects have been considered to be additive to and independent of irradiation; however, recent data have brought this assumption into question. It is certain that corrosion-produced hydrogen does cause significant dimensional changes simply due to the 16-17% difference in density between zirconium hydride and zirconium. A length change of on the order of 0.25% can be induced by 1000 ppm hydrogen in an unirradiated material. Whether or not the presence of hydrides contributes to the mechanisms of irradiation creep and growth is yet to be determined.

Fuel rod diametral changes are caused by stress dependent creep processes. Fuel rod length changes are caused by several phenomena:

- Stress free axial elongation due to irradiation growth.
- Anisotropic creep (before pellet/cladding contact) due to external reactor system pressure. Because of the tubing texture, axial elongation results from creep down of the cladding diameter. In a non-textured material such as stainless steel, creep down of the cladding would only result in an increase in cladding thickness, with no change in length.
- Creep due to pellet-cladding mechanical interaction (PCMI) after hard contact between the cladding and fuel. This occurs in mid-life, depending on the cladding creep properties and the stability of the fuel.
- Hydriding of the cladding due to corrosion.

Bow of a component such as a BWR channel or PWR control rod assembly can occur if one side of the component changes length more than the other side. Such differential length changes occur due to differential stress and creep, to relaxation of differential residual stresses, or to differential growth due to differences in flux-induced fluence, texture, material cold work, and hydrogen content (and, although not usually present, differences in temperature or alloying content).

In the ZIRAT 7 Annual Report the following areas were listed as requiring more data and understanding to assure optimum component performance at the high fluences and burnups currently achieved or proposed for modern fuel designs:

- Factors affecting formation of <c> component dislocations
- Effects of alloying elements such as Nb, Fe and Sn and impurities such as C and S
- Temperature dependence of growth and creep over the full range of operating temperatures
- Long term effects of small residual stresses
- Lack of comparable high fluence data for the variety of new alloys being introduced for corrosion resistance
- Effects due the influence of heat treatment on microchemistry and texture
- Detailed influence of neutron flux and energy spectrum on creep (and perhaps growth, although the current wisdom indicates no effect)
- Effects of hydride orientation and distribution on dimensional changes

To that list must be added understanding of the effect of hydrogen and hydrides on the mechanisms of growth and creep.

In the recent past, the main fuel performance issue in the dimensional stability area has been BWR channel bowing, which interferes with control blade insertion in specific plants, Cheng, 2003. The recent literature indicates that also of importance are PWR assembly bow, performance of newer alloys to moderate burnups, and performance of all alloys at high burnup (a topic which is addressed in detail in the ZIRAT 8 Special Topics Report, High Burnup Issues, 2003). This review examines what the most recent literature says about these and other issues.

## 5.2 EFFECTS OF HYDROGEN

Hydrides have long been known to cause dimensional increases in zirconium alloys, but fuel bundle performance concerns only become obvious with the reports of unusual grid and guide tube assembly growth reported by Kesterson, et al., 2000 and King, et al., 2002. These papers have been reviewed in earlier ZIRAT reports, Adamson and Rudling, 2002 and Adamson and Rudling, 2001. A key feature is illustrated in Figure 5-1 where the effect of hydrogen on dimensions is given for unirradiated Zircaloy measured at room temperature. It is seen that 1000 ppm hydrogen is measured experimentally to cause a dimensional change of about 0.2%, as compared to a theoretical value of about 0.3%. The strains are the same in the longitudinal or transverse directions of highly textured strip or tubing.

## 6 CORROSION AND HYDROGEN UPTAKE

### 6.1 OUT-REACTOR EXPERIMENTATION (BRIAN COX)

In the ZIRAT – 7 Special Report on Corrosion of Zirconium Alloys, Adamson, et al., 2002, the current views of the corrosion and hydrogen uptake mechanisms were presented. The critical steps in the mechanistic assessment can be summarised as follows:

- The only mobile species in the protective oxide next to the metal/oxide interface are oxygen ions and electrons. Potential measurements across such oxide films show significant space charge build-up, and indicate that electron conduction is usually the rate limiting process in thin oxide films at normal reactor temperatures.
- Long-term corrosion rates are determined by the extent of breakdown of the protective oxide film. Several possible mechanisms for this breakdown have been identified, but the relative importance of these has yet to be firmly established. *Inter alia*, these breakdown mechanisms are:
  - Mechanical cracking of the oxide as the high compressive stresses at the oxide/metal interface become progressively tensile near the surface.
  - Shear cracks develop at oxide crystallite boundaries, as a result of the transformation of tetragonal  $\text{ZrO}_2$  (formed near the oxide/metal interface) to monoclinic  $\text{ZrO}_2$  when the compressive stress decreases.
  - Degradation of tetragonal to monoclinic zirconia by exposure to water (or water vapour), leading to development of porosity.
  - Dissolution of the  $\text{ZrO}_2$  crystallite boundaries as a result of  $\text{LiOH}$  concentration in pores and cracks in oxide film because the saturation temperature of the coolant is exceeded under heat flux conditions. The similar concentration of boric acid may be prevented by the large size of borate ions.
  - A similar dissolution of  $\text{ZrO}_2$  in BWRs resulting from the high concentration of peroxide ions in irradiated boiling water.

Other important factors that affect the corrosion rates in operating reactors are:

- a) The thermal conductivity of the oxide film that determines the oxide/metal interface temperature in reactor fuel cladding, and provides a feed-back loop through the temperature at the oxide/metal interface, and the temperature coefficient of the oxide growth process. A secondary feed-back loop may be present if the thermal conductivity of the oxide decreases with increasing oxide thickness and/or increasing oxide temperature at the interface.



- b) In iron containing Zr alloys, the redistribution of iron from some Fe containing intermetallic particles by fast neutron collisions causes enhanced oxide breakdown and accelerated post-transition corrosion. This effect increases with increasing fast neutron dose resulting in a progressive acceleration of corrosion.
- c) Enhanced electronic conduction in the oxide resulting from reactor irradiation can accelerate pre-transition corrosion, and can lead to enhanced localised corrosion (nodular and shadow) in BWRs, where galvanic potential differences with dissimilar metals (extrinsic – i.e. structural or intrinsic – i.e. intermetallics) persist. With high dissolved hydrogen in the water in PWRs these potential differences do not persist.
- d) The absence of evidence for direct irradiation effects in the oxide film (no point defect clusters or dislocation loops seen) explains why pre-transition corrosion rates in-reactor appear to be the same as in the laboratory; except in the early stages of growth, where enhanced electronic conduction results in small oxidation rate increases.
- e) Accumulation of hydride precipitates at the oxide/metal interface under heat flux (once the hydrogen solubility in the metal is exceeded) causes enhanced oxide breakdown, and hence accelerated post-transition corrosion.

There are, therefore, at least five different feed-back loops potentially causing accelerated corrosion of zirconium alloys in-reactor:

- Increasing oxide/metal interface temperatures under heat flux and thickening oxide.
- Increasing corrosion rates as LiOH concentration in oxide increases with boiling.
- Decreasing oxide thermal conductivity with increasing oxide thickness and interface temperature.
- Progressively increasing post-transition corrosion rates due to Fe redistribution by fast neutrons.
- Increased post-transition corrosion rates due to hydride precipitation at interface.

Not all Zr alloys are equally degraded by all these factors.

In order to estimate in-reactor behaviour accurately there needs to be a physically based module addressing each of the above factors in any model. At present only a few of these factors are modelled in this way, some of the others are addressed by data fitting techniques without any realistic knowledge of the response curves, and the rest are ignored. Progress towards more soundly based models is occurring albeit slowly.

While the ultimate aim is a sound understanding of in-reactor behaviour, not all the factors listed above are irradiation dependent, and therefore need to be studied in-reactor. Many can be studied in the laboratory, and some irradiation effects can be simulated with gamma-, electron-or heavy ion irradiation and do not need actual in-reactor measurements. In practice, actual in-reactor observations can be difficult to interpret, because it is not possible to distinguish the critical factors that have led to the observed result. In addition the widespread use of zirconia ceramics in other situations, such as thermal barrier coatings; gate resistors in MOSFETs; and as inert matrix nuclear fuels ensures that other sources of information are available in out-reactor experiments.

To discuss progress in the past year the recently published data will be covered under the following headings:

- 6.1.1 Oxide Properties
- 6.1.2 Oxidation Film Properties
- 6.1.3 Corrosion Tests
- 6.1.4 Irradiation Effects
- 6.1.5 Hydrogen Uptake

#### **6.1.1 Oxide Properties**

During studies of inert matrix fuels based on yttria stabilised zirconia, Degueldre, et al., 2003, some tabulated properties for monoclinic zirconia were given, Table 6-1, and calculated values for the intrinsic thermal conductivity were presented, Figure 6-1. The calculated intrinsic values are higher than reported experimental values (see Adamson, et al., 2002), which are generally in the range  $2 \pm 0.5 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ . For present purposes the interesting feature of the theoretical values in Figure 6-1 is the steep decrease in thermal conductivity with increasing temperature in the 600-700K temperature range. This factor alone will result in a feedback effect as the oxide thickens and the oxide/metal interface temperature increases, and is independent of any decrease in oxide thermal conductivity that may result from increases in the porosity of the thick oxides produced at high burnup. Another study of the thermal conductivity of inert matrix fuel based on ceria stabilised zirconia, Lee, et al., 2003, did not include any data for monoclinic zirconia.

## 7 WATER CHEMISTRY IMPACT ON FUEL PERFORMANCE (PETER RUDLING)

Historically, water chemistry has impacted fuel performance through AOA and/or excessive fuel clad corrosion in most cases in relation to CRUD fuel clad deposition. However, neither AOA nor fuel clad excessive corrosion is only a result of the water chemistry. In both AOA and fuel clad excessive also fuel rod duty is a crucial parameter and in the latter case, also fuel clad microstructure has a major impact on corrosion.

The current trend in both PWRs and BWRs tends to increase the corrosion duty due to more aggressive core loading and higher discharge burnups. Concurrently, the coolant water chemistry is being modified to reduce plant activity build-up and decrease the cracking tendencies in reactor internals. Examples of water chemistry changes for BWRs are: HWC, Zn-injection<sup>10</sup>, Fe-injection, O-injection, NMCA<sup>11</sup>. For PWRs the corresponding changes are: increased maximum LiOH concentration<sup>12</sup>, increased maximum boron coolant concentration (for longer cycles), Zn-injection. To improve the corrosion resistance of the fuel clad materials, the fuel vendors are modifying their current fuel clad product for BWR applications while new materials (ZIRLO and M5) have been developed for PWRs.

More details of the different water chemistry changes and the potential impact on fuel performance are treated in the ZIRAT-8 Special Topical Report, entitled: The effects of Zn-injection (PWRs and BWRs) and Nobel Metal Chemistry (BWRs) on fuel performance – an update”. The interested reader is also referred to the ZIRAT-6 Special Topical Report, entitled: Water Chemistry and Crud Influence on Cladding Corrosion”.

Table 7-1 and Table 7-2 lists the most recent cases of accelerated corrosion in PWRs and BWRs.

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<sup>10</sup> Zinc injection in PWRs is believed to extend the life of the SGs, by mitigating IGSCC cracking, and to reduce dose rates from the RCS during outages

<sup>11</sup> Platinum (Pt) and Rhodium (Rh) are added to the BWR reactor water during plant shutdown to coat the system surfaces with Pt and Rh for 48 hours, Cheng, 2002. NMCA process results in about one atomic layer of noble metals (Pt + Rh) on stainless steel surfaces. About 5 to 10 times more Nobel Metals, NMs, are found in the crud on fuel rod surfaces. The benefit of NMCA is that only a small amount of hydrogen addition (~0.25 ppm) in feed water is needed to protect stainless steel components against stress corrosion cracking. The reduced hydrogen addition will reduce the offgas activity in the main steam line. NMs re-circulate within the reactor water loop during operation and re-application may be needed every 2-3-fuel cycles.

<sup>12</sup> Higher pH is desirable to reduce crud transport/release to lower outage dose rates.

Table 7-1: Summary of previous PWR failure key events.

Nuclear unit	Cycle, year	Comment
TMI-1	Cy 10, 1995 <sup>13</sup>	<ul style="list-style-type: none"> <li>Nine Zr-4 Cladding fuel rods failed after 122 days of operation. All failed and degraded pins reportedly had DCP Distinctive Crud Pattern <sup>14</sup></li> <li>High peaking factors, thermal-hydraulic conditions. Calculations indicated that no boiling should have occurred on the pins with DCP, although the pins with DCP were calculated to have a slightly higher temperature.</li> <li>Water chemistry (low pH at BOC, pH &lt; 6.9, max LiOH 2.2 ppm)</li> <li>Some AOA effect was found reaching a maximum in the middle of cycle 10.</li> <li>The source of the crud could not be determined. The crud sampling showed that the nickel-to iron ratio was in the range 1.25 to 16.7.</li> </ul>
Seabrook	Cy 5, 1997	<ul style="list-style-type: none"> <li>Five one-cycle ZIRLO rods failed</li> <li>Longer cycle in transition to 24-month cycle</li> <li>Possibly crud-induced overheating resulting in substantial nucleate boiling</li> </ul>
Palo Verde 2	Cy 9, 2000 <sup>15</sup>	<ul style="list-style-type: none"> <li>Eleven failed one-cycle Zr-4 (OPTIN cladding) rods. Primary defect in span 8-9, secondary hydrides in span 2-4</li> <li>AOA was experienced early in cycle 9. A mid-cycle shutdown produced a reversed AOA situation, i.e. the previously low relative power in the upper core now had a significantly higher than predicted power resulting in fuel failures 3 months after the MCO. All but one was a high-duty peripheral rod, and significant tenacious crud deposits were observed in grid spans 7 – 9 on all rods.</li> </ul>

<sup>13</sup> For more details, see section 5.6.2 in ZIRAT-6 Special Topical Report, “Water Chemistry and Crud Influence on Cladding Corrosion”, by G. Wikmark and B. Cox.

<sup>14</sup> This acronym implies that the fuel inspection revealed crud deposits on the fuel rod and that the deposits were uneven in the rod circumference

<sup>15</sup> See section 9.2.1.1 in ZIRAT-6, Annual Report for more details.

Table 7-2: Summary of previous BWR failure key events.

Nuclear unit	Cycle, year	Comment
KKL	1997, 1998 <sup>16</sup>	<ul style="list-style-type: none"> <li>Excessive Shadow Corrosion on LK II Zr-2 Cladding under the Inconel x-750 grid springs. The oxide thickness was locally above 500 <math>\mu\text{m}</math>. The most notable cladding corrosion attacks were found on fuel that had experienced a fourth, fifth, or sixth operational cycle.</li> <li>Zn-injection</li> <li>Low level of Fe in coolant</li> </ul>
River Bend	Cy 8, 1999 <sup>17</sup>	<ul style="list-style-type: none"> <li>At least 12 First cycle fuel rods were failed GE11, Zr-2 Cladding P6.</li> <li>Heavy crud - The failures appeared in bundles with a significant iron crud deposition. The heavy deposits almost filled the gaps between the fuel rods. Some 700 pounds (320 kg) iron was estimated to have been input to the River Bend-1 RPV during cycle 8 (1998-1999). Crud deposit thickness in the range 37 – 55 mils (940 – 1400 <math>\mu\text{m}</math>) was reported. Analysis of the crud showed that the major phases were hematite and spinel, reportedly magnetite or zinc ferrite. Significant amounts of copper, up to 15% was found in some cases.</li> <li>No NMCA</li> <li>Zn-injection</li> </ul>
Vermont Yankee	Cy 22, 2001 - 2002	<ul style="list-style-type: none"> <li>Noble Metal Chemical Addition, NMCA was injected in April 2001 (RFO 22)</li> <li>No HWC was applied</li> <li>Admiralty Brass Condensers and consequently elevated Zn and Cu coolant concentrations exist.</li> <li>Visual examination at MOC showed that 5 GE13B 2nd Cycle Fuel - Barrier fuel/P6 cladding had failed in four assemblies due to elevated corrosion. All failed fuel were part length rods, PLR, from the same material tub lot “A”, that was characterised by low Fe content (but within specification). The results prompted VY to replace all fuel assemblies in the core containing material tube lot “A” and other assemblies that had been subjected to the most sever corrosion duty in previous cycles.</li> </ul>

<sup>16</sup> For more details, see section 5.8 in ZIRAT-6 Special Topical Report, “Water Chemistry and Crud Influence on Cladding Corrosion”, by G. Wikmark and B. Cox.

<sup>17</sup> For more details, see section 5.9 in ZIRAT-6 Special Topical Report, “Water Chemistry and Crud Influence on Cladding Corrosion”, by G. Wikmark and B. Cox.

## **8 ZIRCONIUM ALLOY MANUFACTURING (PETER RUDLING)**

### **8.1 INTRODUCTION**

The development of manufacturing of the zirconium alloys has, during the last years, been characterised by decreased variation in process parameters, to cope with higher demands on the materials; increased efficiency, in order to reduce manufacturing costs; and introduction of new materials, again to comply with higher demands on the cladding.

In all these cases, it is important to be aware of the possible influence of the changes on materials properties not in focus for the change of the process or the new alloy introduced. For instance, a change to improve the corrosion properties by alloying with niobium may change the mechanical properties during power ramp, i.e. that the same PCI rules may not apply.

### **8.2 NEW RESULTS**

*The new results are summarised in the sequel. Some papers both related to alloy microstructure and manufacturing are treated in section 3.*

#### **8.2.1 Calandria tubes**

*Thin walled calandria tubes for pressurised heavy water reactors are normally manufactured either by seam welding of Zircaloy-4 sheets or by a seamless process route.*

In a study by Kapoor, et al., 2003, the effect of calandria tubes manufacturing process, Figure 8-1, on texture, microstructure hydriding behaviour and residual stress was investigated. In addition, the mechanical anisotropy developed due to seam welding was investigated. The results show that the microstructure of the base metal of seam welded tube was found to be similar to the seamless tube microstructure, Figure 8-2, with a typical martensitic structure observed in the heat affected and the fusion zone.

*Figure 8-3 indicate that the basal and pyramidal pole texture in the parent material of seam welded tube was somewhat different to that of the seamless material.* Residual stress analysis in the longitudinal and transverse direction, TDs, showed that the residual stresses in the seamless tubes were more uniform compared to that of the tube subjected to seam welding, Figure 8-4. *The residual stresses will relax during in-pile irradiation as a result of stress relaxation through creep and may result in (un-wanted) dimensional changes of the product. In general, larger residual stresses in larger material volumes results in larger dimensional changes. It is not clear from the residual stress analysis done in this study if these tubes will undergo significant dimensional changes and if so if there will be a difference in magnitude of changes of the seamless and seamwelded tube.* The authors also reported that, the deformation mechanism acting during the contractile strain ratio, CSR<sup>18</sup>, measurements in the Base Material, BM, and the Heat Affected Zone, HAZ, was twinning on  $(11\bar{2}2)$  plane and slip on  $(01\bar{1}0)$  plane in the Fusion Zone, FZ. The resulting CSR values of BM and FZ were almost isotropic in width and thickness directions, whereas anisotropy in the CSR values were observed in HAZ.

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<sup>18</sup> CSR test results correlates with the mechanical properties which in turn is a result of the texture. A material specimen is subjected to a tensile test and the plastic deformation in two directions are measured and the CSR value is the ratio between the plastic deformation in these two different directions. A non-textured material show a CSR value of 1 since plastic deformation is equal in the two measured directions, while a CSR value different from 1 indicate a textured material.



Figure 8-1: Processing methods (Route 1 - seam welding or Route 2 - by a seamless process) adopted for the manufacturing of thin walled calandria tubes, Kapoor, et al., 2003.



## **9 PRIMARY FAILURE AND SECONDARY DEGRADATION (PETER RUDLING)**

### **9.1 INTRODUCTION**

#### **9.1.1 Primary Failures**

During reactor operation, the fuel rod may fail due to a primary cause such as fretting, PCI, manufacturing defects, corrosion, etc., Table 9-1.

Table 9-1: Primary failure causes for LWR fuel during normal operation and anticipated operational occurrences.

Primary Failure Cause	Short Description
Excessive Corrosion	An accelerated corrosion process results in cladding perforation. This corrosion acceleration can be generated by e.g. CRUD deposition (CILC <sup>19</sup> ), enhanced spacer shadow corrosion, ESSC, <sup>20</sup> (in BWRs), dry-out due to excessive fuel rod bowing.
Manufacturing defects	Non-through-wall cracks in the fuel cladding developed during the cladding manufacturing process. Defects in bottom and/or top end plug welds. Primary hydriding due to moisture in fuel pellets and or contamination of clad inner surface by moisture or organics. Too large gap between the fuel rod and the spacer grid supports (poor spacer grid manufacturing process) leading to excessive vibrations in the PWR fuel leading to fretting failures. Chipped pellets may result in PCI failures both in liner and non-liner fuel
PCI	Pellet Cladding Interaction-an iodine assisted stress corrosion cracking phenomenon that may result in fuel failures during rapid power increases in a fuel rod. There are three components that must occur simultaneously to induce PCI and they are: 1) tensile stresses- induced by the power ramp, 2) access to freshly released iodine-occurs during the power ramp, provided that the fuel pellet temperature becomes large enough and 3) a sensitised material – Zircaloy is normally sensitive enough for iodine stress corrosion cracking even in unirradiated state.
Cladding collapse	This failure mechanism occurred due to pellet densification. This failure mode has today been eliminated by fuel design changes and improved manufacturing control.
Fretting	This failure mode has occurred due to: Debris fretting in BWR and PWR Grid-rod fretting - Excessive vibrations in the PWR fuel rod causing fuel failures. This situation may e.g. occur due to different pressure drops in adjacent fuel assemblies causing cross-flow. Baffle jetting failures - Related to unexpectedly high coolant cross-flows close to baffle joints

<sup>19</sup> Crud Induced Localised Corrosion – an accelerated form of corrosion that have historically resulted in large number of failures in BWRs. Three parameters are involved in this corrosion phenomenon, namely: 1) Large Cu coolant concentrations- as a result of e.g. aluminium brass condenser tubes, 2) Low initial fuel rod surface heat flux – occurs in Gd rods and 3) Fuel cladding that shows large initial corrosion rates- occurs in cladding with low resistance towards nodular corrosion.

<sup>20</sup> This corrosion phenomenon resulted recently in a few failed rods. The mechanism is not clear but seems to be related to galvanic corrosion. This corrosion type may occur on the fuel cladding in contact or adjacent to a dissimilar material such as Inconel. Thus, this accelerated type of corrosion occurred on the fuel cladding material at spacer locations (the spacer springs in alloy BWR fuel vendors fuel are made of Inconel). Water chemistry seems also play a role if the fuel cladding material microstructure is such that the corrosion performance is poor. Specifically coolant chemistry with low Fe/(Ni-Zn) ratio seems to be aggressive (provided that the cladding material shows poor corrosion performance. A fuel cladding material with good corrosion resistance does not result in ESSC, enhanced spacer shadow corrosion, even in aggressive water chemistry.

*The failure statistics for US plants up to the year 2001 were reported by Cheng, 2002, Table 9-2, Table 9-3 and, Table 9-4. For BWRs, about 30 % of the failures during the time period of 1991 to 2001 were due to corrosion (CILC/ Crud) and 26 % were due to debris fretting failures. For PWRs, 40 % of the failed assemblies during the same time period were due to grid-rod fretting, and 17 % were related to debris fretting. In the year 2001, 40 out of 48 failed assemblies (83 %) in the 58 EDF PWRs were related to grid-rod fretting, Table 9-5.*

Table 9-2: BWR failure root causes in US plants. The table shows the number of failed rods, Cheng, 2002.

Cause	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	Total
CILC							6	46					52
Crud/Corrosion									14			X	14
Fabrication	1	2	1	2									6
PCI		1	2		2	6	1	1				X	13
Debris	20	2	6	4		5	3	5	6	2	2	2	57
Uninspected	3	7	5	9	2	8	1	1		16			52
<b>Total</b>	<b>24</b>	<b>12</b>	<b>14</b>	<b>15</b>	<b>4</b>	<b>19</b>	<b>11</b>	<b>53</b>	<b>20</b>	<b>18</b>	<b>2</b>	<b>24+</b>	<b>214</b>

Table 9-3: PWR failure root causes in US plants. The table shows the number of failed assemblies, Cheng, 2002.

Cause	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	Total
Handling Damage	2	1		1	1		2			1			8
Debris	67	23	14	6	11	1	9	3	2		3		139
Grid Fretting	9	34	36	9	20	36	21	57	45	35	16		318
Primary Hydriding		4								1			5
Crud/Corrosion					4		4			7			15
Clad Creep Collapse					1								1
Other Fabrication	1	6	3	3	16	5			1	1			36
Other Hydraulic						18							18
Inspected/Unknown				2			5	1	1				9
Uninspected	34	55	49	37	21	14	19	2	12	7			250
<b>Total</b>	<b>113</b>	<b>123</b>	<b>102</b>	<b>58</b>	<b>74</b>	<b>74</b>	<b>60</b>	<b>63</b>	<b>61</b>	<b>52</b>	<b>19</b>	<b>?</b>	<b>799</b>

## 10 CLADDING PERFORMANCE UNDER ACCIDENT CONDITIONS (PETER RUDLING)

### 10.1 INTRODUCTION

Three different design basis accidents are treated in this section: (i) Loss Of Coolant Accident, LOCA, (ii) Anticipated Transient Without Scram, ATWS, and, (iii) Reactivity Initiated Accident, RIA.

#### 10.1.1 LOCA

The objectives of the Emergency Core Cooling System, ECCS, LOCA criteria are to maintain core coolability and preserve heat transfer area and coolant flow geometry during the quench phase and post-quench phase of a LOCA. The criteria in most countries are:

- Peak Cladding Temperature, PCT,  $< 1204^{\circ}\text{C}$  (or  $2200^{\circ}\text{F}$ )
- Equivalent Cladding Reacted, ECR<sup>35</sup>,  $< 17\%$
- Hydrogen gas produced  $< 1\%$ <sup>36</sup>.
- Fuel must have coolable geometry<sup>37</sup>.
- Core temperature maintained at low value for extended time<sup>38</sup>.

The first two criteria are addressing clad embrittlement. An embrittled fuel cladding could potentially result in loss of fuel coolable geometry due to fuel clad rupture during the post-LOCA oxidation phase.

The existing LOCA criteria were established in the 1973 ECSS Rule-Making Hearing and the development of the criteria were nicely reviewed by Hache and Chung, 2001 and summarized in the following.

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<sup>35</sup> The ECR is defined as the total thickness of cladding that would be converted to stoichiometric  $\text{ZrO}_2$  from all the oxygen that are contained in the fuel cladding as  $\text{ZrO}_2$ , and oxygen in solid solution in the remaining clad metal phase. Subsequently, in the NRC Information Notice 98-29 (August 3, 1998), the NRC stated that total oxidation, as mentioned in 10 CFR 50.46 (acceptance criteria for LOCA analysis), includes both preaccident oxidation and oxidation occurring during a LOCA.

<sup>36</sup> Total amount of hydrogen shall not exceed 1% of the hypothetical amount generated by the reaction of all the zirconium in the fuel cladding with the water/steam.

<sup>37</sup> The coolable geometry may be lost by either fuel clad ballooning causing coolant channel blockage or fuel cladding fragmentation due to clad embrittlement.

<sup>38</sup> After any operation of the ECCS, the core temperature shall be maintained at an acceptably low value and decay heat removed for the extended period of time required by long-lived radioactivity.

At the 1973 ECSS Rule-Making Hearing, the Atomic Energy Commission, AEC, staff and commissioners and OECD-GSNI specialists were of the opinion that retention of clad ductility was the best guarantee against potential fragmentation of fuel cladding during post-LOCA. This potential fragmentation could occur due to not-so-well-quantified loading, such as thermal shock, hydraulic, and seismic forces, and the forces related with handling and transportation. *Later also the forces due to pellet-cladding bonding has been identified as a significant force during post-LOCA.*

The Equivalent Cladding Reacted, ECR and Peak Clad Temperature, PCT, criteria were based on retention of clad ductility at 275°F (135°C, the saturation temperature during reflood) according to slow ring compression tests of double-sided steam oxidation non-ballooned unirradiated cladding Zircaloy-2 and -4 samples. The selection of the 17% ECR value was specific to the use of the conservative Baker-Just clad oxidation correlation. However, if a best-estimate correlation would have been used instead such as e.g. Cathcart-Pawel correlation, the threshold ECR would have been <17%. Most countries are using this criterion for ensuring adequate cladding ductility. In some countries it is assumed that the largest clad tensile stress<sup>39</sup>, during post-LOCA, is due to the thermal stresses during the quenching phase during the LOCA. In these countries the post-LOCA clad ductility criterion is specified such that the fuel cladding must be capable to withstand the quenching stresses without rupturing (which normally is a transversal break of the fuel cladding). Both in Russia and in Japan, the maximum allowable ECR during a LOCA transient is specified to ensure that the cladding can survive such a quenching without rupturing. In Russia a maximum value of 18% ECR is used for Zr1Nb claddings assessed in quench tests without any constraints of the clad during quenching. In Japan a corresponding value of 15% are used for Zircaloy claddings but assessed in quenching tests with significant constraints of the fuel clad.

During the late 70's – early 80's, slow ring-compression tests of ballooned and bursted samples showed that the 1973 criteria failed to ensure retention of ductility at 135°C in narrow local regions near the burst opening<sup>40</sup>, where H content exceeds about 700 ppm. This phenomenon was not known in 1973. However, the 1973 criteria still ensured resistance to 0.3 J impact tests, and survival after fully constrained quench tests for low-burnup Zircaloy<sup>41</sup>. The implications of the results, are such that for high-burnup fuel cladding tubes with a H uptake, prior to the LOCA event, exceeding about 700 ppm:

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<sup>39</sup> During a LOCA, such as ballooning of the rod near the spacer grid, rod-grid spring chemical interaction and the friction between the fuel rod and spacer grids can restrict the axial movement of the cladding thus imposing clad tensile stresses during reflooding. In recognition of this, the AEC Staff wrote during the 1973 Rule-Making Hearing that “the loads due to assembly restraint and rod-to-rod interaction may not be small compared to the thermal shock load and cannot be neglected”. Subsequently, it was concluded that: “The staff believes that quench loads are likely the major loads, but the staff does not believe that the evidence is as yet conclusive enough to ignore all other loads”. *The NRC position is still that the best way to ensure that the fuel cladding will not fragment during post-LOCA event is to retain clad ductility since it may be difficult for codes to calculate exactly the post-LOCA stresses in the cladding*, Meyer, 2002.

<sup>40</sup> It appears that the stagnant conditions of water/steam in this location will significantly increase the hydrogen pickup during LOCA clad oxidation.

<sup>41</sup> Following these results, Japan modified the basis of its ECR criterion to ensure survival after fully constrained quench tests by specifying a maximum of ECR 15%.

- the 17% ECR criterion may fail to ensure retention of ductility at 135°C and,
- the clad will not survive a fully constrained quench test without rupturing while it may survive an unconstrained quench test.

Also, the 1204°C peak cladding temperature (PCT) limit was selected on the basis of slow-ring compression tests that were performed at 25-150°C. However, samples oxidized at 1315°C are far more brittle than samples oxidized at 1204°C in spite of comparable level of total oxidation. This is because oxygen solid-solution hardening of the prior-beta phase is excessive at oxygen concentrations >0.7wt%. Consideration of potential for runaway oxidation (*due to that the oxidation process of the Zirconium material becomes to exothermic to be cooled by water*) was a secondary factor in selecting the 1204°C limit. The 1204°C limit was subsequently justified by the observations from impact tests and handling failure of fuel rods exposed to high temperatures in the Power Burst Facility. The 1204°C PCT and the 17% ECR limits are inseparable, and as such, constitute an integral criterion. The post-quench ductility and toughness of the cladding material are determined primarily by the thickness and the mechanical properties of the transformed-beta layer.

The LOCA sequence can be divided into three phases, Figure 10-1:

- Ballooning and burst of the cladding occur since the rod internal pressure becomes much higher than the system pressure of the reactor pressure vessel and strength of the fuel cladding decreases as the temperature increases.
- The cladding is oxidized by steam and it becomes brittle when severely oxidized.
- The embrittled cladding may rupture by thermal shock caused by rapid cooling during the reflooding stage.

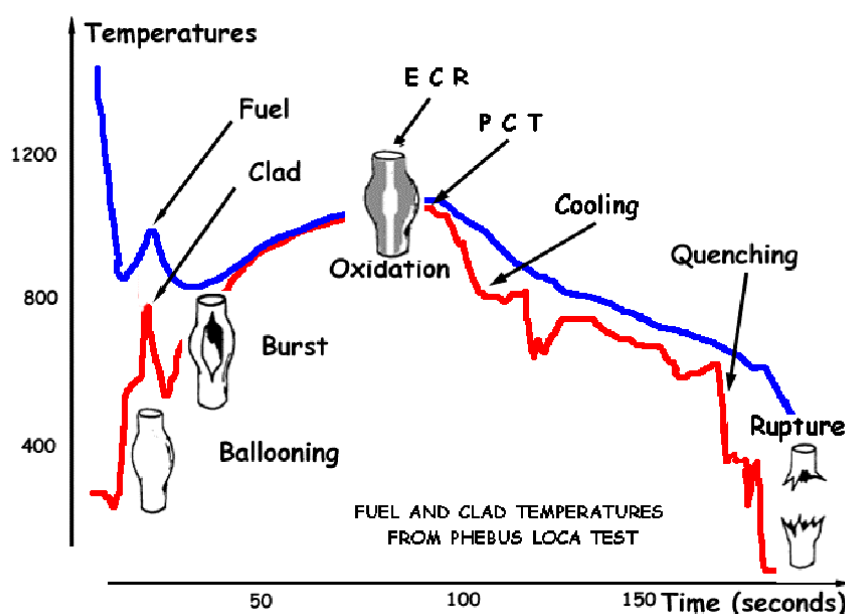


Figure 10-1: PWR LOCA cycle, Maillat, et al., 2001.

## **11 SPENT FUEL PERFORMANCE CRITERIA DURING INTERMEDIATE STORAGE AND TRANSPORTATION**

### **11.1 INTRODUCTION**

The fuel related dry storage licensing issues have been significantly modified starting last year and are continuing to do so during the current year. Emphasis has also shifted to the evaluation of the fuel behavior during transportation and handling accidents and the development of criteria that will assure that the Codes of Federal Regulations (CFRs) will be met under the hypothetical accident conditions.

The issues related to wet storage of spent fuel have not changed since the review made in 2001 and the reader is referred to the ZIRAT-6 report for that information.

Potential permanent storage sites have been identified, but have not been completely evaluated and licensed in the US or any other country with a need to store spent fuel. The *US Yucca Mountain site* has been approved by the Congress and Senate, but the projected date for receiving spent fuel at that site is currently “officially” 2010 at the earliest, a date that even knowledgeable NRC personnel doubt will be met. The long and uncertain time period before the Yucca Mountain site is ready and the likely extension of that date forces the utilities into an intermediate storage mode. The uncertainties of the permanent storage schedules in turn, make the long term planning by the utilities difficult.

All of the US utilities will fill up their wet storage space by about 2013 and by then will need intermediate storage facilities, almost exclusively on-site dry storage casks. An exception might be the licensing of an off-site dry cask storage facility such as Skull Valley (discussed later), or the expansion of wet storage facilities may not be out of the question. The longer cooling times required in wet storage for high burnup fuels before they can be loaded into dry casks may result in a net increase of assemblies over the number of fuel assemblies saved by the high burnup operation, thus filling up the pool more rapidly than expected. One such European utility operating on MOX cores that require significantly longer cooling times than UO<sub>2</sub> cores is expanding the wet rather than the dry storage facilities.

The currently licensed US dry storage facilities, or Independent Spent Fuel Storage Installations (IFSIs), increased by 5 during the past year for a total of 27; their locations are shown in Figure 11-1. An additional 15 sites are likely to become licensed in the near future; the location of 14 sites are shown on Figure 11-2 and an additional one not shown is the Brunswick site.

An intermediate, *away-from-reactor (AFR) dry storage site at Skull Valley*, Utah is in the licensing stage. Sponsored by a consortium of utilities that formed the Private Fuel Storage (PFS) group, the site is located on the reservation of the Skull Valley Band of Goshute Indians east of Salt Lake City in a truly desolate location. Since the NRC SER in 2002 concluding that the facility would be safe and meet regulatory requirements and several hearings by the Atomic Safety and Licensing Board (ASLB) the issue of an F-16 fighter aircraft crash into the facility from a nearby air force base was brought up. Proof of the probability of less than one event in a million per year is required by the ASLB. The meeting on this topic is postponed from December 2003 to early 2004 in order to give PFS time to answer additional questions raised by the NRC on this topic some as recently as October, 2003. The NRC must give their case to ASLB at the same time PFS presents their data. The proposed dry cask storage capacity of Skull Valley has been reduced during the negotiations of the past year from 4000 to about 300 to satisfy various concerns.

A ruling by ASLB would come earliest in mid-2004 and if favorable one would expect numerous appeals. If there were none, construction could start at the end of 2004. Completion would take 2 years, so that receipt of fuel could not occur prior to 2007.

There is still no ruling on the State of Utah's appeal to the 10<sup>th</sup> District Federal Court of Appeals on the District Court of Utah's decision that the prohibitive, outrageous laws passed by the State to stop Skull Valley are unconstitutional.

Essentially *all countries that operate nuclear power plants have licensed dry storage facilities* by now, since none have permanent storage facilities that are licensed. The countries in Europe include Belgium, Bulgaria, Czech Republic, Germany, Hungary, Italy, Netherlands, Rumania, Russia, Slovakia, Spain, Switzerland, Ukraine and in Asia they include Japan.



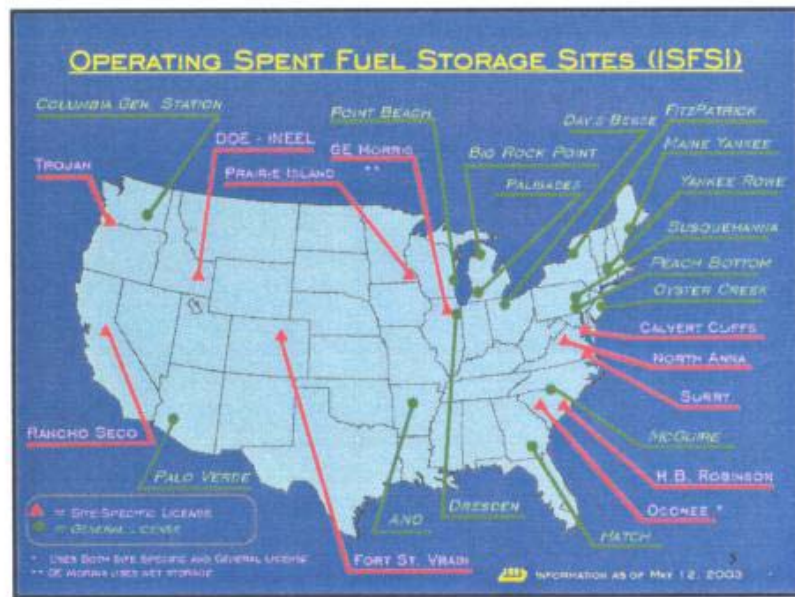


Figure 11-1: Brach, 2003



Figure 11-2: Brach, 2003

## 12 POTENTIAL BURNUP LIMITATIONS

### 12.1 INTRODUCTION

The potential fuel assembly burnup limitations related to zirconium alloy components are summarised in this Section. The burnup limitation that have actually been reached, but have been or are being extended, are:

- Corrosion of Zry-4 in high power PWRs, extended by improved cladding alloys. However, improved corrosion performance by the new alloys may allow the utilities to use the added margins, to modify plant operation e.g., to lower fuel cycle cost. This modified operation will in most cases result in higher corrosion duty of the zirconium materials. Thus, it is believed that the corrosion will always be limiting for plant operation even with the new type of alloys.
- Bowing of PWR fuel assemblies contributed in part by irradiation growth, creep and hydriding of Zry-4, extended by improved guide tube materials (i.e., lower irradiation growth and hydriding rates), and reduced assembly holdown forces, but not yet finally eliminated. It is questionable, whether design changes to make the fuel assembly stiffer will resolve the issue. It may be that these design changes will only increase the incubation time before bowing occurs and at that point it will be even more difficult to e.g. insert control rods.
- Bowing of BWR channels, extended by improved manufacturing processes, design changes such as variable wall channel thickness with relatively thicker corners, and in-core channel management programs,
- RIA and LOCA related burnup licensing limits, in the process of being assessed by additional experimental data and analyses. Based upon the on-going test program, it is not clear today if the licensing limits will be extended or not. The limits may also actually be reduced.

The categories of event likely to eventually limit reliably and safely achievable burnup levels are outlined below. The zirconium alloy component most sensitive to the limits and potential methods for extending the limits are noted below.

## 12.2 CORROSION AND MECHANICAL PROPERTIES RELATED TO OXIDE THICKNESS AND H PICKUP

- BWRs: increased uniform and shadow corrosion, oxide thickness spalling.--- due to longer residence time, higher power and water chemistry changes. Current crucial issues are: shadow corrosion mechanisms, CRUD-chemistry-corrosion interaction and specific effects of NMCA with or without Zn-injection.
- PWRs: increased uniform corrosion, oxide thickness, spalling --- due to longer residence time and higher Li, higher power, more boiling. The introduction of Zr-Nb alloys may also result in accelerated corrosion at the welds, e.g., between the end-plugs and cladding tubes. Also, welding between dissimilar metals such as e.g. ZIRLO and Zry-4 may result in chemical compositions of the welds that show inferior corrosion resistance. Luckily, the corrosion temperatures at these elevations in the core is significantly lower than the peak temperatures and this may be the reason that no corrosion issues have been reported so far in the welds.
- Increased H pickup tendency<sup>54</sup>:
  - decreased ductility and fracture toughness during any situation (e.g., RIA, PCMI, LOCA and post-LOCA events, seismic event, transport container drop-accident conditions)
  - increased corrosion due to impact of hydrides at the cladding outer surface
  - may impact creep behaviour of fuel claddings during class 1-IV events and during intermediate storage.
  - Increased knowledge of the effects of irradiation and hydrides on the fracture toughness of thin-walled zirconium alloy components needed.

### Most sensitive component

Spacer and fuel claddings

### Increase margin for PWR

- Improved knowledge of corrosion and hydrogen pickup mechanisms,
- Improved alloys with appropriate fabrication processes: ZIRLO/E635 (Anikuloy), M5/Zr1Nb. Duplex is another alternative that may be necessary to achieve satisfactory mechanical properties
- Change to enriched B soluble shim to reduce Li. There is however a fear that enriched B would increase AOA potential, i.e., more absorption per g. B, even though there may be less B.
- Improved water chemistry and CRUD control
- Increase corrosion resistance of steam generator materials

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<sup>54</sup> due to the introduction of more corrosion resistant materials. For some types of Zr alloys, the hydrogen pickup fraction increases with decreasing corrosion rate.

Increase margin for BWR

- Improved knowledge of corrosion and hydrogen pickup mechanisms,
- Improved alloys under development
- Modification of manufacturing processes (to get optimum sized, more stable second phase particles)
- Improved water chemistry and CRUD control

*12.3 DIMENSIONAL STABILITY*

- Increased growth of components and differential growth between them resulting in reduced fuel rod spacing or even rod contact, guide tube bowing, fuel assembly bowing, spacer cell and envelope dimensions, BWR fuel channel and PWR fuel assembly bow may result in
  - decreased thermal margins (LOCA and dry-out)

Most sensitive component

Potentially all zirconium alloy components, but currently PWR guide tubes and BWR channels. Also BWR spacers have occasionally increased so much in dimensions that unloading of the assembly from the outer channel was very difficult.

Increase margin for PWR

- Alloys with lower growth and hydriding rates for guide tubes – ZIRLO, M5, M4, E635 (Anikuloy)
- Lower hold-down forces
- Beta-quenched material after the last plastic deformation step during manufacturing. Beta-quenched materials do normally, however, show higher corrosion rate and lower ductility. These properties may be improved by an appropriate final heat-treatment in the alpha-phase.

Increase margin for BWR

- Uniform microstructure and texture throughout the fuel outer channel
- Beta-quenched material in as-fabricated step
- Channel management programs
- More corrosion resistant material in channels and spacers is allow irradiation for longer cycles
- Increased understanding of basic phenomena driving the channel bow process.

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