

A preliminary assessment of the long-term storage of AP1000 spent fuel

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Issue 1

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EXECUTIVE SUMMARY

This report reviews the present understanding of the effects of reactor operations and reactor chemistry on the stability of AP1000 spent fuel assemblies during long-term storage. The work is applied to UK storage options for spent fuel arising out of a new-build reactor programme based on Westinghouse's AP1000 pressurised water reactor.

Specific aspects relevant to pond storage include a review of degradation mechanisms operating in LWR fuel assemblies, and a view is offered as to which of these mechanisms may be operating during long-term storage which would prevent safe storage for up to 100 years. The limited data available suggest that general corrosion rates of zirconium alloys and stainless steel are very low and pose no threat to component integrity over the storage times required. Due to in-reactor effects, fuel cladding ductility will be reduced, but no further change is expected to occur at pond storage temperatures. With specific regard to fuel ponds operating at high pH, due to the possible co-location of PWR and AGR fuel, it is noted that corrosion rate data for zirconium alloys in caustic solutions is extremely limited. The data that are available suggest a maximum corrosion rate in caustic pond water of [REDACTED] microns per year, implying [REDACTED] microns metal loss during 100 years storage. The other possible feature of ponds including co-located AGR and PWR fuel is the addition of corrosion inhibitors such as nitrate ions. No corrosion rate data for zirconium alloys in nitrate solutions have been found. However, it is considered reasonable to assume that corrosion rates are unchanged from those in demineralised water. It is recommended that further data should be obtained or commissioned on corrosion of zirconium alloys in pond storage conditions. In particular, data on caustic or nitrate dosed pond water should be sought.

Specific aspects relevant to dry storage (including the pre-storage assembly drying) include a review of degradation mechanisms for LWR fuel assemblies, with similar considerations of which mechanisms may be operating over long-term storage and which would influence safe storage for up to 100 years. Specific issues considered include clad creep, localised corrosion of sensitised stainless steel, and hydride attack of irradiated zirconium alloys. Calculations using NNL's ENIGMA fuel performance code have indicated that [REDACTED]

[REDACTED]. However, the ENIGMA calculations assumed no crud formation on the cladding surface, and a sensitivity study suggested that [REDACTED]. It is considered that irradiation conditions will be borderline for the possible onset of radiation induced sensitisation (RIS) in stainless steel, which could render the components vulnerable to attack by nitric acid (formed by radiolysis of moist air). However, the probability is that RIS conditions will not be met, and the likelihood of this mechanism occurring is therefore low. With respect to zirconium alloy components, the re-orientation into a radial geometry of zirconium hydride platelets formed during irradiation can lead to embrittlement or delayed hydride cracking, both of which can threaten component integrity. However, the probability of structural component failure by this means is considered low, and ENIGMA calculations indicate that [REDACTED]

[REDACTED] Firmer conclusions on dry storage can generally only be drawn once dry storage and assembly drying systems are defined, when more rigorous calculations are recommended. However, the out-of-pile creep behaviour of the ZIRLO™ cladding alloy, including any annealing of irradiation damage at temperature, and any hydrogen hardening, should first be clarified, and it is recommended that a calculation is performed to more definitively assess the susceptibility of the assembly top nozzle to radiation induced sensitisation.

VERIFICATION STATEMENT

This document has been verified and is fit for purpose. An auditable record has been made of the verification process. The scope of the verification was to confirm that: -

- The document meets the requirements as defined in the task specification/scope statement
- The constraints are valid
- The assumptions are reasonable
- The document demonstrates that the project is using the latest company approved data
- The document is internally self consistent

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1. Introduction

The UK Health and Safety Executive (HSE) is currently undertaking a Generic Design Assessment (GDA) of the PWR designs being offered as new-build power plant for the UK. Various parts of the assessment work programme have been subcontracted to competent organisations. The component of the GDA that is of interest here is determining whether there is confidence that the spent fuel can be safely retrieved, transported and disposed of at the end of post-irradiation storage.

The UK National Nuclear Laboratory (NNL) is engaged to support HSE as an adviser on spent nuclear fuel storage and disposal, with particular emphasis on the effects of reactor operations and reactor chemistry on the behaviour of the fuel assemblies during long-term storage prior to disposal.

This report constitutes a preliminary assessment of the long-term storage of spent fuel from Westinghouse's AP1000 pressurised water reactor. The scope is described in Section 1.1.

1.1. Assessment scope

The assessment covers the behaviour of the AP1000 spent fuel assemblies during long-term wet or dry storage for a nominal period of 100 years. The aim is to evaluate the integrity of the fuel rod cladding and assembly structural components, and, in particular, to determine whether or not these elements remain sufficiently intact to allow later retrieval, transport and disposal of the assemblies. The effects of the irradiation, initial pond storage, and any assembly drying (prior to dry storage) on the state of the fuel assemblies prior to long-term storage are included in the assessment. Only standard UO₂ fuel is considered — the effects of using mixed oxide (MOX) fuel would require further assessment. The cladding material is assumed to be the standard (~ 1% tin, cold-worked stress-relief annealed) version of Westinghouse's ZIRLO™ zirconium alloy, as per Westinghouse's GDA submittal and the relevant HSE Step 3 report (AR 09/040-P). However, since optimised ZIRLO™ (with a reduced tin content of ~ 0.5% and a partially recrystallised microstructure) is the current Westinghouse product, the mass production of fuel that would be required for AP1000 build, and the timeframes of the fuel manufacture, suggest that it would, in fact, be optimised ZIRLO™ that is used in a UK AP1000. Where appropriate, the effects of this are noted in this report.

A nominal initial pond storage period of ten years is assumed, but the effects of shorter and longer periods of five and fifteen years are also considered. The maximum assembly average burnup is taken to be 65 GWd/tU for consistency with final geological disposal assumptions.

The work programme in which this report was written has been divided into a number of tasks as per the agreed proposal. These are listed below.

- **Task 1:** kick-off meeting at Bootle to agree and finalise the scope of the work.
- **Task 2:** define a detailed list of information required from the Requesting Parties in order to carry out the assessment.
- **Task 3:** where detailed information is not available, the NNL will estimate relevant input parameters for the models or validate models provided by the Requesting Parties.
- **Task 4:** undertake a review of fuel acceptance criteria following long-term storage. Where appropriate the NNL will engage with the Radioactive Waste

Management Directorate (RWMD) of the NDA. Consideration of possibly damaged fuel will be discussed.

- **Task 5:** carry out decay heat versus time calculations using FISPIN for input into the corrosion assessments where required.
- **Task 6:** perform calculations using ENIGMA, and wet storage corrosion models, to estimate clad oxide thickness, creep (due to rod overpressure) and stress for the different storage alternatives. In addition, discuss the propensity for cladding failure due to grid-to-rod fretting. Hence, estimate the timescales over which cladding integrity can be maintained. Both 18 and 24 month cycles will be considered, as well as initial pond storage periods from 5 to 15 years.
- **Task 7:** undertake a short review of the corrosion behaviour of the assembly structural component materials (other than the fuel rod cladding).
- **Task 8:** undertake a short assessment of the corrosion of the assembly structural components (other than the fuel rod cladding) using the information from Task 7.
- **Task 9:** undertake a short set of calculations to estimate conditions prevailing in crud, namely the Li/B concentrations and clad temperature. A range of crud thicknesses and possible conditions will be considered. In addition the possible impact of Zn addition will be discussed.
- **Task 10:** undertake a short series of ENIGMA calculations of corrosion film thickness examining the effects of alternative reactor water chemistry regimes and the effect of fuel crud.

Tasks 1 and 2 have already been performed. The later tasks are described in the remaining sections of this report. The description of the estimation of relevant input parameters (Task 3) is incorporated into the discussions on the other tasks.

The kick-off meeting (Task 1) was held on the 8th September 2009 and attended by three NNL representatives ([REDACTED]). A summary of the meeting was drafted and issued to HSE [1.1].

With respect to Task 2, a list of information was produced by NNL and issued to HSE for consideration [2.1]. Some material was subsequently supplied by HSE, but several aspects requested are not currently available. Best estimate assumptions have therefore been used where necessary in this assessment. The key information that is not available is that concerning: (i) details of the dry storage systems and conditions; and (ii) details of the fuel drying procedures and conditions.

2. Review of fuel acceptance criteria following long-term storage (Task 4)

The UK fuel acceptance criteria for disposal following long-term storage that would apply to AP1000 spent fuel are understood to have not yet been defined by the NDA's Radioactive Waste Management Directorate (RWMD). Since the acceptance criteria will also be country, repository and transport cask design specific to a significant extent, it was not considered worthwhile to review LWR fuel acceptance criteria experience in other countries in order to predict potential criteria that would apply. Instead, a review of licensing criteria for LWR fuel long-term storage was performed, since it is these licensing criteria which ultimately prevent failure of the fuel rods during storage and therefore give fuel which is acceptable for disposal. Only dry storage licensing criteria were considered, because those applicable during wet storage would be expected to be primarily the same as those applicable during initial pond storage, which are outside the scope of this report.

The key licensing guidelines that are available are those issued by the American (USNRC) and German (RSK) regulators [4.1, 4.2]. No UK guidelines are known to exist. Guidelines in other countries are generally identical, or very similar, to these key guidelines. The most important, or primary, limits (which apply to both the dry storage itself and the pre-storage assembly drying) are those imposed on cladding hoop stress and hoop strain.

Concerning clad stress, limiting hoop stress values of 120 and 90 MPa are imposed in the German and US guidelines, respectively. The aim is to prevent formation of radial hydrides in the cladding, which can promote either severe embrittlement or delayed hydride cracking (DHC)*. The German limit is based on experiments on irradiated Zircaloy cladding, while the US limit is conservatively based on experiments on unirradiated Zircaloy cladding. Since the USNRC guidelines also quote a stress threshold for formation of radial hydrides in irradiated clad of 120 MPa, the German limit is preferred. Westinghouse have noted the applicability of the 90 MPa (unirradiated clad) limit to standard ZIRLO™ [4.3]. From the arguments above, it can therefore be inferred that the 120 MPa limit is also applicable to standard (but not necessarily to optimised) ZIRLO™ cladding. However, further evidence would be required from Westinghouse to confirm this.

Concerning clad strain, the German guidelines quote a 1% hoop strain limit. The aim is to prevent excessive clad creep that could lead to rupture. Recent experimental studies have shown that the real ductility of irradiated Zircaloy is actually somewhat greater than indicated by the limit [4.2], but nevertheless 1% is currently applied universally as a failure criterion for Zircaloy under all circumstances, including in-reactor operation. ZIRLO™ irradiated to 68 GWd/tU has been shown to have a ductility of greater than 2% [4.3], so given the similarity of the burnup to the 72 GWd/tU value being considered here, the 1% limit can also be conservatively applied to ZIRLO™ cladding. Some ambiguity exists in application of the limit, in particular whether: (a) it should be applied relative to as-manufactured conditions, or relative to post-irradiation dimensions; and (b) it should apply to the creep strain or the total permanent (creep plus growth) strain. UK practice in the case of in-reactor licensing is to treat the limit as a permanent hoop strain relative to as-manufactured dimensions, since this should be consistent with strain data used to calculate the limit. This is also therefore assumed here.

* During dry storage, the initially high clad temperatures (see Section 4.3) cause dissolution of the circumferentially oriented zirconium hydride platelets formed during irradiation. Hydrides then re-precipitate as the clad temperatures gradually reduce during storage due to decay heat reduction. The orientation of the re-precipitated platelets is primarily dependent upon the clad hoop stresses — below some threshold stress the orientation tends to be circumferential, whereas above the threshold stress the orientation tends to be radial.

Other limits included in the USNRC guidelines are a (normal operation) clad temperature limit of 400°C and a limit on the number of thermal cycles of ten, with a maximum 65°C change in temperature during each cycle. The clad temperature limit helps prevent excessive clad creep that could cause rupture, while also helping prevent radial hydride formation by limiting cladding hoop stresses and the amount of soluble hydrogen available in the cladding. The thermal cycling limits are because such cycling (which is most likely to occur during vacuum drying of assemblies, where several evacuation / inert gas backfill cycles are possible) enhances the formation of radial hydrides. Since the clad temperature and thermal cycling limits help prevent clad creep rupture and radial hydride formation, which are more directly prevented by the primary limits on clad stress and strain, they can be classified as secondary limits.

3. Decay heat versus time calculations (Task 5)

In order to calculate the decay heat output pertinent to AP1000 fuel, cross-section library files were created and subsequently used in FISPIN [5.1] inventory calculations. Two such calculations were performed to determine the decay heat output from: (i) an AP1000 assembly with the maximum assembly average discharge burnup of 65 GWd/tU; and (ii) the peak burnup pin from the same assembly. The assembly type is assumed to be that with the maximum enrichment undoped fuel and minimum number of integral fuel burnable absorber (IFBA) rods (which would be most likely to achieve the highest burnups), i.e. the 4.45% enriched assembly with 72 IFBA rods [5.3].

Burnup dependent cross-sections were first calculated using the neutron lattice code CASMO-4 [5.2] together with fuel design parameters sourced from the Westinghouse design control document [5.3]. The neutronic code CASMO-4 is specifically designed for LWR application and is used by the majority of nuclear utilities around the world that operate BWRs or PWRs.

In reality, the peak pin burnup will depend on the assembly average burnup attained as well as the core loading strategy, with assemblies irradiated in a region with a higher neutron flux gradient having a larger difference between the peak pin and assembly average burnup. For the purposes of this study, the peak pin burnup has been assumed to be 10% higher than the assembly average value, giving a peak pin burnup of 72 GWd/tU. This burnup is judged to be conservative, since in reality fuel performance limitations and neutronic optimisation will ensure the core designer would opt to rotate assemblies to ensure the spread in pin burnup and power is as low as possible.

The main characteristics of the two FISPIN runs performed are summarised in Table 1. The resulting decay heat output (in W/tHM) versus time for the two runs over the initial 500 year cooling period are plotted in Figure 1. A corresponding plot over the initial 10 year cooling period is included as Figure 2.

Table 1: Summary of FISPIN runs performed

	Assembly	Peak burnup pin
Burnup (GWd/tU)	65	72
Power density (kW/kgU)	40.2	44.5
Fuel type	17x17, 264 fuel pins, UO ₂ / UO ₂ -IFBA	As assembly run
Undoped fuel enrichment (wt%)	4.45	4.45

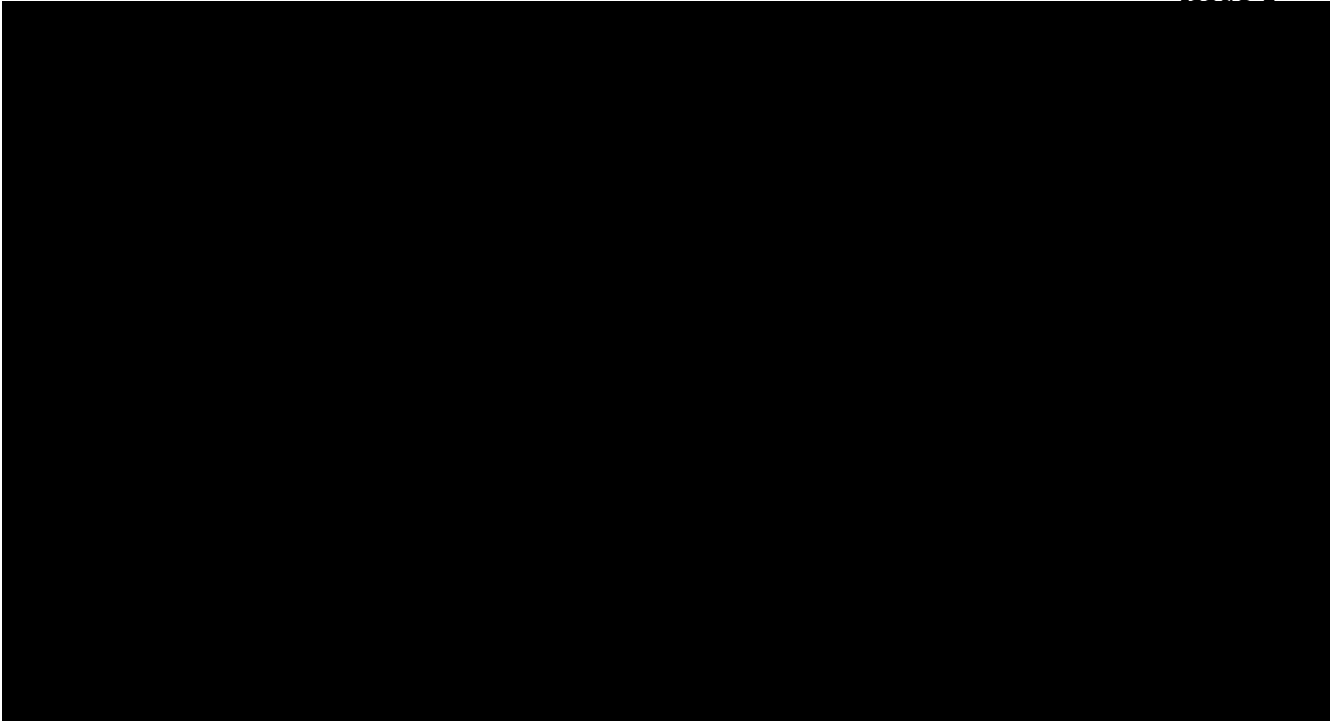


Figure 1: Decay heat versus time for 65 GWd/tU AP1000 assembly and corresponding peak pin over initial 500 year cooling period

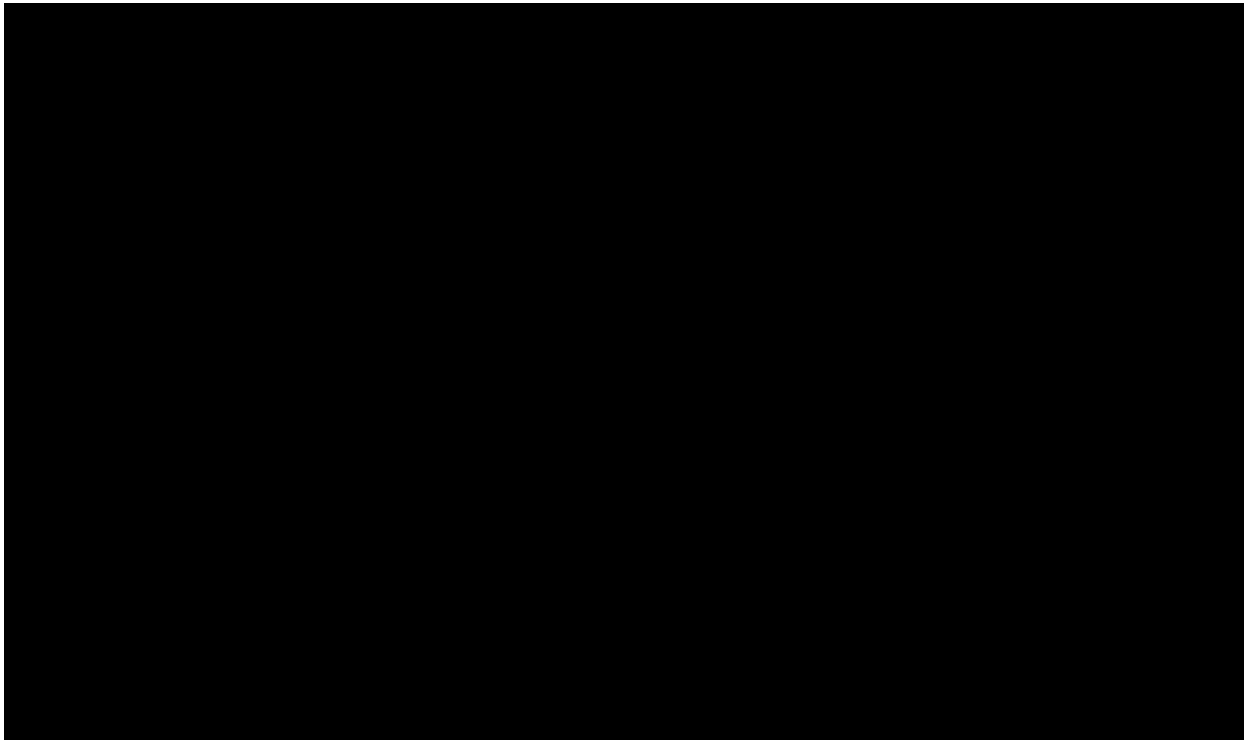


Figure 2: Decay heat versus time for 65 GWd/tU AP1000 assembly and corresponding peak pin over initial 10 year cooling period

4. Cladding behaviour during long-term storage (Task 6)

The fuel rod cladding behaviour during both wet and dry long-term storage is considered in this section. More specifically, the thermo-mechanical behaviour of the lead (maximum burnup) rod in an assembly with the maximum assembly average burnup of 65 GWd/tU is determined. The assembly type assumed is as per the decay heat calculations (see Section 3). The behaviour during the preceding irradiation is first evaluated to determine the probable mechanical state of the rod prior to storage. The timescales over which clad integrity can be maintained are then estimated.

Due to its maximum burnup characteristic, the lead rod will be a rod without an IFBA coating, and is modelled as such. However, due to the helium release associated with the zirconium diboride depletion, it is possible that the end-of-life rod internal pressure in an IFBA rod could actually be higher than that in the lead rod, and therefore that an IFBA rod could potentially be limiting with respect to clad integrity during long-term storage. Due to the way in which the lead rod power history is modelled, with the rod average power set to a through-life value that gives an end-of-life rod internal pressure at power equal to the coolant pressure (see Section 4.1), this is not an issue here.

Calculations are performed using NNL's ENIGMA fuel performance code [6.1, 6.2, 6.3]. Starting from the as-manufactured condition, ENIGMA calculates the evolution of the thermo-mechanical state of an LWR fuel rod over time. ENIGMA is internationally recognised as a state-of-the-art code with a proven pedigree. It has been used, amongst other applications, to license the BNFL fuel for the initial charge and first three reloads of the Sizewell B PWR.

The ENIGMA calculation of the evolution of the thermo-mechanical state of a rod involves modelling a large number of phenomena. These include: (a) standard phenomena associated with thermo-mechanical behaviour of the fuel and cladding materials, e.g. heat transfer by conduction, convection and radiation, thermal expansion, creep, elasticity, and plasticity; (b) phenomena related to the presence of a neutron flux, e.g. cladding axial growth, radial power depression, helium generation and release; (c) phenomena related to fissioning, neutron capture and the generation of fission products, e.g. the generation and release of fission gas (Xe and Kr), fuel densification, and fuel swelling; (d) phenomena related to microstructural changes in the fuel, e.g. formation of high burnup structure, and grain growth; (e) phenomena related to radial temperature gradients in the fuel pellets, e.g. pellet wartsheafing, and axial extrusion and dish filling; (f) chemical phenomena, e.g. clad corrosion, crud formation, and helium absorption. Many fuel and cladding properties, e.g. fuel thermal conductivity, and phenomena, e.g. cladding corrosion, are also fast flux, fast fluence or burnup dependent.

4.1. Cladding state after irradiation

The cladding state of the lead rod after irradiation is estimated using ENIGMA. The standard ZIRLO™ cladding material is nominally modelled, but the effects of instead using optimised ZIRLO™ (with all other parameters unchanged) are also investigated. No crud formation is modelled — this is consistent with Westinghouse claims for no crudding in the AP1000 [1.1]. (However, the effects of crud formation are investigated under Task 10 — see Section 8.) The ENIGMA input parameters include the geometry and fabrication details of the fuel pellets, cladding and fuel rod, assembly design characteristics, reactor operating conditions, and the fuel rod powers versus time (or power history). The active fuel stack is divided into ■ axial zones for computational purposes; power versus time information is therefore provided for each of these ■ zones. With the exception of the power history, the parameter values used are listed in Table 2, together with the references from which they were taken. The majority of the

data (listed in black) come from documentation provided by Westinghouse. The remaining data (listed in red) were obtained from other sources, or were estimated based on NNL experience (with a consequent introduction of uncertainty into the calculations) [6.4].

Westinghouse’s GDA submittal assumes an AP1000 fuel assembly type which is their standard 17x17 XL Robust design modified to include four intermediate flow mixing grids in the top mixing vane grid spans. The ENIGMA calculations performed are therefore strictly only applicable to this assembly type.

Table 2: ENIGMA input parameters

ENIGMA Parameter	Value	Reference(s)
<i>Fuel Characteristics:</i>		
Enrichment (weight fraction)	0.0445	[6.5] Table 4.1-1
Fuel mean linear intercept (MLI) grain size (m)	██████	
Fuel porosity (volume fraction)	0.045	[6.5] Table 4.1-1
Pellet dish radius (m)	██████	
Dish:pellet volume ratio	██████	
Chamfer:pellet volume ratio	██████	
Pellet length (m)	9.83E-3	[6.5] Table 4.1-1
Pellet outer radius (m)	4.096E-3	[6.5] Table 4.1-1
Fuel stack active length (m)	4.2672	[6.5] Table 4.1-1
<i>Cladding and Rod Characteristics:</i>		
Rod internal pressure (MPa)	████	
Gas composition (He,N ₂) (mole fractions)	████	
Upper plenum volume (m ³)	██████	
Lower plenum volume (m ³)	██████	
Clad inner radius (m)	4.178E-3	[6.5] Table 4.1-1
Clad outer radius (m)	4.75E-3	[6.5] Table 4.1-1
Clad initial hydrogen content (ppm)	██	ENIGMA default
<i>Assembly Design and Reactor Operating Conditions:</i>		
Heat generated in fuel (fraction of total)	0.974	[6.5] Table 4.1-1
Fast flux per unit rating (n/m ² /s per kW/kgHM)	██████	
Coolant pressure (MPa)	15.513	[6.5] Table 4.1-1
Sub-channel coolant mass flow rate (kg/s)	0.30	[6.5] Table 4.1-1
Sub-channel hydraulic diameter (m)	11.78E-3	[6.5] Table 4.1-1
Sub-channel flow area (m ²)	8.55E-5	[6.5] Table 4.1-1
Coolant cycle-averaged lithium concentration (ppm)	██	ENIGMA default
Coolant temperature at inlet (°C)	279.44	[6.5] Table 4.1-1

The UO₂ fuel pellet material properties are simulated using the default models in ENIGMA. The ZIRLO™ cladding properties are modelled as described below (with T representing the absolute temperature in Kelvin). With the exception of clad corrosion, both standard and optimised ZIRLO™ are modelled identically. This is consistent with the design aim for optimised ZIRLO™, which was to retain the mechanical behaviour of standard ZIRLO™ (most importantly the creep and growth) while improving the corrosion resistance. That this was achieved is supported by the almost identical rod diameter axial profiles of standard and optimised ZIRLO™ rods irradiated as part of the Westinghouse/EDF Advanced Precursor Assembly (APA) programme after one cycle of irradiation [6.6].

- Clad density = [REDACTED] kg/m³ (from [6.7] Appendix A).
- Clad specific heat capacity = [REDACTED] kJ/kg/K (default ENIGMA value for Zircaloy-4 — [6.7] Appendix A shows that the specific heat capacity of ZIRLO™ and Zircaloy-4 are virtually identical up to 700°C).
- Clad elastic modulus (MPa) = [REDACTED] (default ENIGMA expression for Zircaloy-4 — [6.7] Appendix A supports modelling the elastic modulus of ZIRLO™ using the same formulation as for Zircaloy-4).
- Clad Poisson's ratio = [REDACTED] (default ENIGMA value for Zircaloy-4 — [6.7] Appendix A supports modelling the Poisson's ratio of ZIRLO™ using the same value as for Zircaloy-4).
- Clad axial growth strains are taken to be [REDACTED]% of those calculated using the ENIGMA model for Zircaloy-4. The [REDACTED]% multiplier gives the best fit to the axial growth strain versus burnup data for both standard and optimised ZIRLO™ from [6.6] — see Figure 3. It is also the best estimate multiplier recommended by Westinghouse [6.7].
- Clad radial and circumferential growth strains are calculated from the axial growth strains and clad radial, circumferential and axial texture factors of [REDACTED], [REDACTED] and [REDACTED] respectively (default ENIGMA values for Zircaloy-4).
- Clad hydrogen pickup fraction = [REDACTED] (default ENIGMA value for Zircaloy-4, since pickup fractions for Zircaloy-4 and ZIRLO™ are known to be comparable [6.8]).
- Clad corrosion for standard ZIRLO™ is simulated using the ENIGMA model [6.9].

[REDACTED]

Clad corrosion for optimised ZIRLO™ is simulated as per standard ZIRLO™, but with a [REDACTED] multiplier applied [REDACTED] [6.6]. Scoping calculations have indicated that both the standard and optimised ZIRLO™ corrosion models give predictions in line with the latest open literature oxide thickness versus burnup data [6.6].

- Clad coefficient of thermal expansion = [REDACTED] K⁻¹ (default ENIGMA value for Zircaloy-4 — [6.7] Appendix A supports modelling the thermal expansion of ZIRLO™ identically to that of Zircaloy-4).
- Clad unirradiated [REDACTED] yield stress at room temperature and clad yield stress dependence on fast fluence and temperature modelled as per Zircaloy-4 (since unimportant during steady-state conditions simulated).
- Clad instantaneous plasticity and thermal creep are modelled as per Zircaloy-4 (since these are unimportant in the steady-state conditions simulated).
- Clad irradiation creep strains are taken to be [REDACTED]% of those calculated using the ENIGMA model for Zircaloy-4. The [REDACTED]% multiplier is as recommended by Westinghouse [6.7].
- Clad thermal conductivity (kW/m/K) = [REDACTED] (function proposed by Westinghouse [REDACTED] [6.10]).

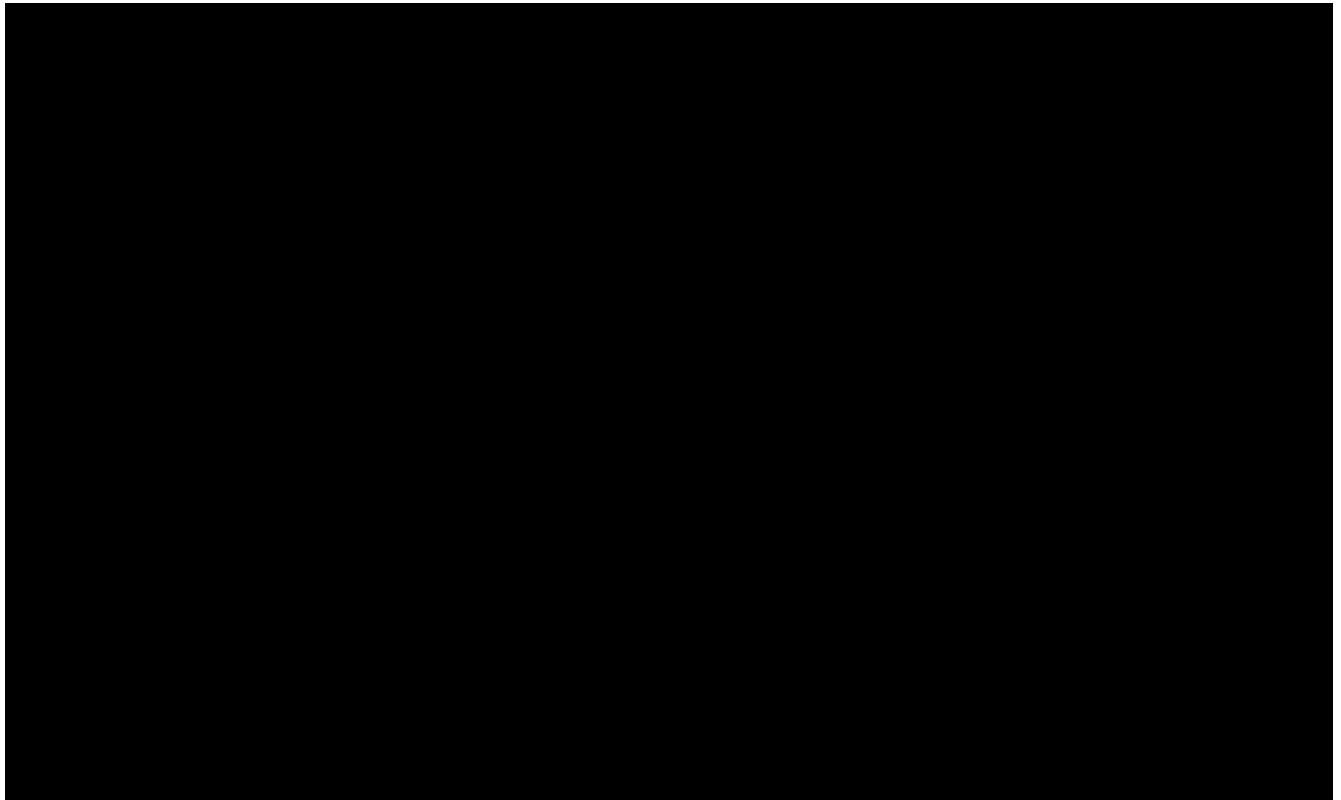


Figure 3: Axial growth strain versus burnup for ZIRLO™: measurements and predictions

A hypothetical three-cycle power history is modelled with equal irradiation times in each cycle and 60 day shutdowns between cycles. The end-of-life rod average burnup is fixed at 72 GWd/tU for consistency with the decay heat calculations (see Section 3). An unchanging axial (relative) power profile is used throughout — in the absence of further information, the typical fourth cycle profile for a 157 assembly, 12 ft PWR core in Figure 4.3-16 of the Westinghouse design control document [6.5] is used (this is expressed in the form relative power versus relative height, and so can readily be scaled to the 14 ft AP1000 core on this basis). The rod average power is set to the through-life value of ██████ kW/m which gives an end-of-life rod internal pressure at power equal to the coolant pressure (with standard ZIRLO™ cladding). Modelling a constant rod average power throughout life generally gives a lower power early in life and a higher power later in life than would occur in reality (due to fuel depletion). This approach should be close to limiting from the point of view of clad corrosion, since the effects of corrosion enhancement due to thermal feedback across the oxide layer will be more significant later in life due to the thicker oxide layers at this time. This, coupled with the conservative nature in terms of the rod internal pressure[†], should be enough to make this suitably conservative overall.

[†] The Westinghouse design criterion with respect to rod internal pressure is that 'the maximum internal pressure of the fuel rod will not exceed the value which would cause the fuel-clad diametral gap to increase during steady-state operation' [6.5]. The limiting value (or design limit) is therefore the pressure that will give a clad creepout rate equal to the fuel swelling rate. Hence, the pressure limit is somewhat larger than the coolant pressure, and rods with internal pressures greater than the coolant pressure are therefore theoretically possible. However, the inclusion of a lower plenum in the AP1000 fuel design, which will significantly increase rod internal pressure margin, together with the conservatism inherent in fuel licensing, mean that simulating a lead rod with an end-of-life internal pressure equal to the coolant pressure is still considered to be conservative.

The bulk coolant temperatures for each axial zone are calculated by ENIGMA using an isolated subchannel thermal-hydraulics model (which gives conservatively high results). The corresponding clad surface temperatures are then determined using the Dittus-Boelter (forced convection) or Thom (nucleate boiling) correlations for the convection heat transfer coefficient. The end-of-cycle (EOC) clad surface temperature predictions are plotted in Figure 4. The resulting clad oxide thickness predictions are plotted in Figure 5 for both the standard ZIRLO™ (solid lines) and optimised ZIRLO™ (dashed lines) cladding materials. The improved corrosion resistance of the optimised ZIRLO™ material is apparent. The peak oxide thicknesses at EOC1, EOC2 and EOC3 are approximately [REDACTED] [REDACTED] microns for standard ZIRLO™, and [REDACTED] [REDACTED] microns for optimised ZIRLO™. These are all comparable to, or slightly lower than, the latest available open literature data from currently operating PWRs at rod average burnups of 24, 48 and 72 GWd/tU [6.6]. The reason for this is that the conservatism (with respect to clad corrosion) of the hypothetical constant through-life power operation modelled is approximately offset by the considerably lower coolant inlet and outlet temperatures for the AP1000 than for currently operating PWRs.

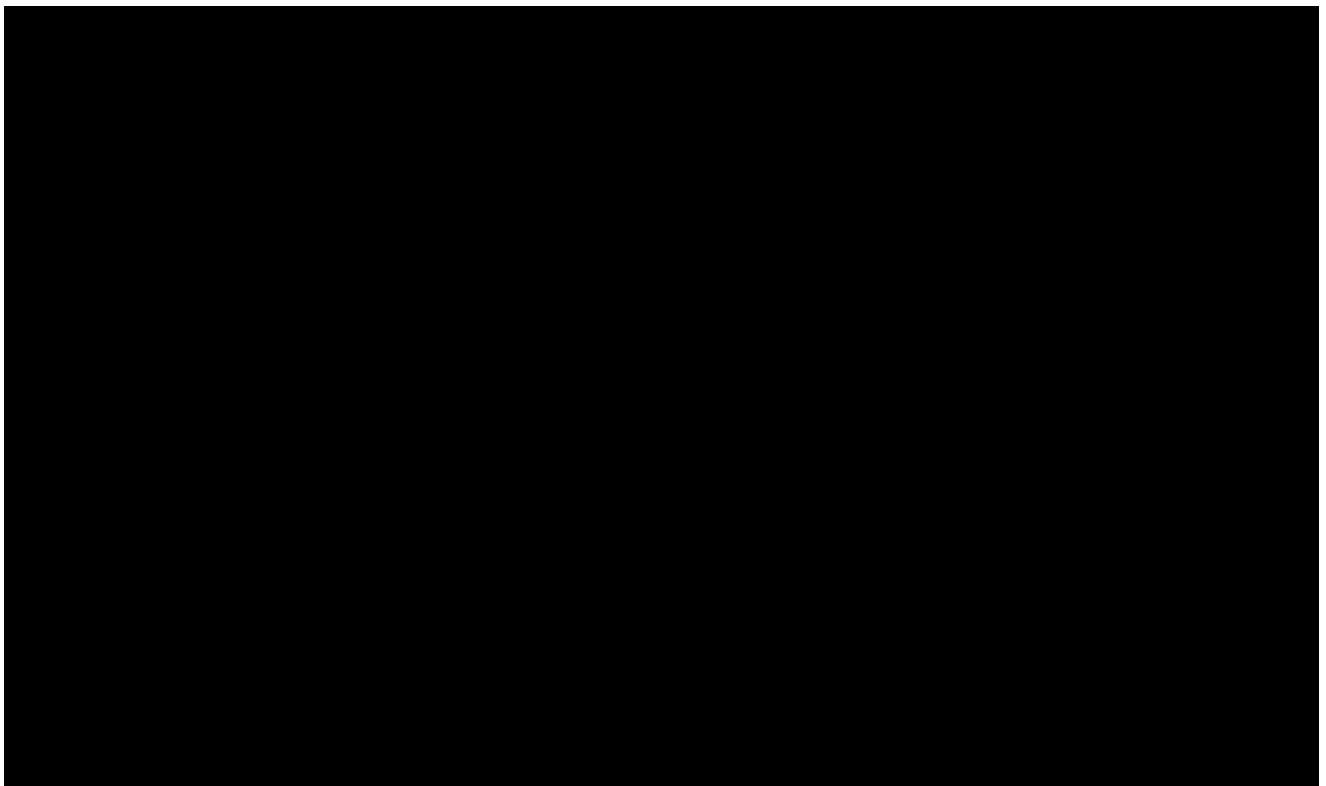


Figure 4: Axial profile of clad surface temperature

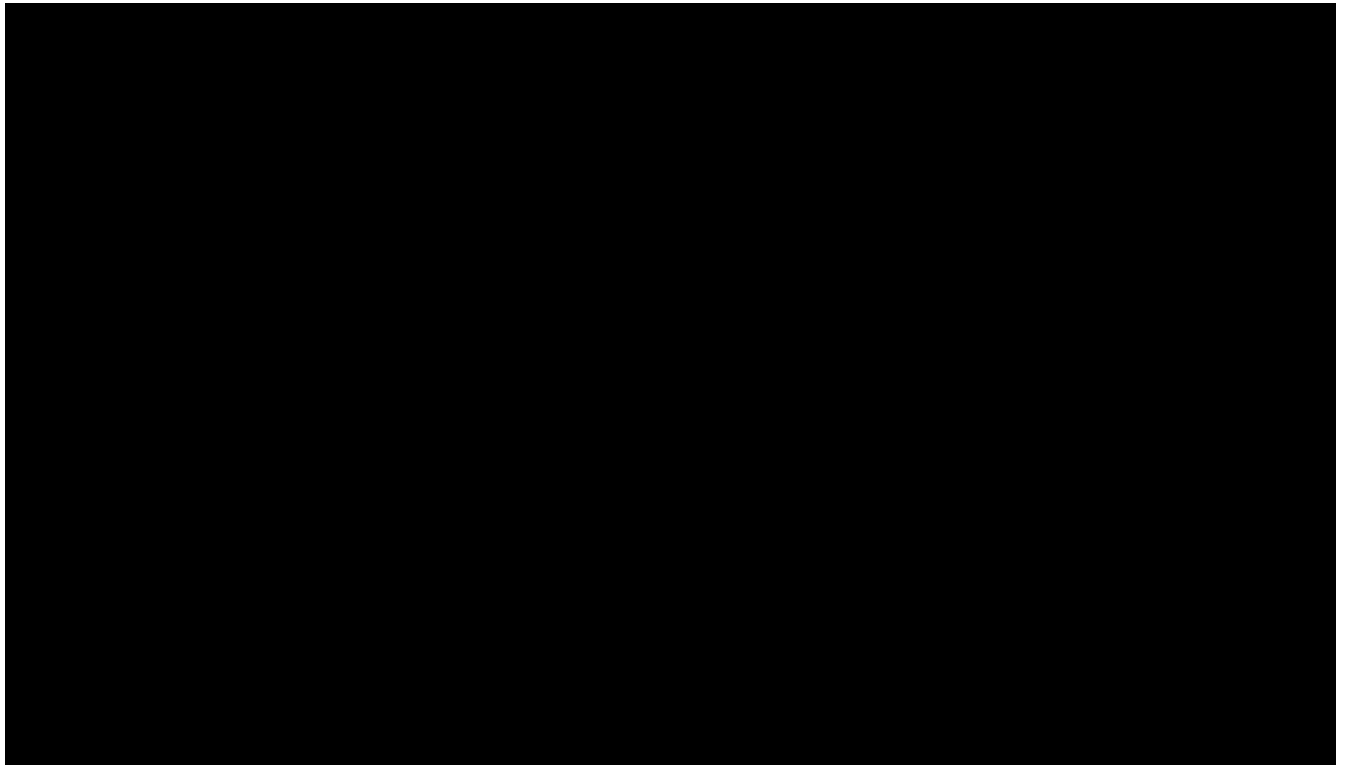


Figure 5: Axial profile of clad oxide thickness for both standard and optimised ZIRLO™ (solid and dashed lines, respectively)

Grid-to-rod fretting wear may occur if flow-induced assembly vibration leads to relative motion between the grid straps and the fuel rods (although the aim is to eliminate this possibility by good fuel assembly design, i.e. maintaining sufficient forces between grid straps and fuel rods by use of grid springs and dimples, and by optimising grid profiles to minimise vibrations). This is not modelled by ENIGMA due to its stochastic nature. However, a maximum fretting wear depth of 10% of the clad wall thickness is typically applied as a design criterion during PWR fuel licensing and this is shown to be met based on operational experience. There is no reason to believe that a similar approach is not possible with AP1000 fuel, especially since the Robust Fuel Assembly design proposed for use in the AP1000 was developed, amongst other reasons, to improve grid-to-rod fretting performance [6.6] (and has so far been successful in doing so — there have been no occurrences of fuel rod leakers due to grid-to-rod fretting during irradiation of over 11,000 Robust Fuel Assemblies in 38 plants [6.6]). Thus, grid-to-rod fretting can be ignored in design calculations such as the one described here.

Debris-induced fretting wear of cladding is also possible. However, the debris filter bottom nozzle and protective grid in the AP1000 assembly design should ensure that the probability of debris-induced fretting wear is negligible.

The ENIGMA calculation described above predicts that the lead rod (and by inference all other rods) will not fail during irradiation. However, what was not simulated includes: stochastic failure mechanisms (such as grid-to-rod and debris-induced fretting); any accident scenarios; any manufacturing defects.

[REDACTED]



4.2. Wet storage

Prior to drying, the fuel assemblies will be in an aqueous pond environment. The conditions in the pond — that is stagnant water, clad temperatures of below 60°C (the design value for the AP1000 spent fuel pond water temperature during normal refuelling is 60°C [6.5]), and the absence of a fast neutron flux — mean that corrosion in this environment will generally be negligible (primarily because the corrosion rate is strongly temperature dependent). The exception to this is if the oxidation is exacerbated by dissolved salts or other solutes, but the controls on pond chemistry should preclude this. Thus, the pond storage should cause no additional corrosion to that which has already occurred under irradiation. This is supported by wet storage experience [6.12]. More detailed evidence is provided in the discussion on corrosion of zirconium alloy materials in Section 5.2.2.

Given the low powers (decay heat only) and clad surface temperatures relative to in-pile values, no fission gas release, helium release or clad creep are expected during pond cooling. Hydrogen diffusion in the cladding is also negligible, and the zirconium hydride platelets formed during irradiation (by reaction of the cladding with the hydrogen produced in the clad oxidation reaction) are stable [6.12].

In conclusion, given suitable controls on pond chemistry, there are no credible phenomena that could occur during long-term wet storage that would challenge the integrity of the fuel rod cladding, even over storage periods of up to 100 years.

4.3. Dry storage

4.3.1. Description of ENIGMA analysis

The ENIGMA analysis of the lead rod irradiation described in Section 4.1 was extended to include a long-term (100 year) dry storage simulation. This included simulation of the pre-storage spent fuel pond cooling and assembly drying. (The combination of spent fuel pond cooling, assembly drying and dry storage is henceforward referred to as post-irradiation operations.) Use of ENIGMA for such an extended simulation has prior pedigree (including the study of dry storage of MOX fuel from the Unterweser PWR for a period of 80 years [6.13]).

The relatively high clad temperatures and high rod internal pressures (due primarily to in-pile release of fission gas from the fuel pellets to the rod free volume) during dry storage and the pre-storage assembly drying result in permanent creep deformation of the cladding over time. The creep strains can be enhanced in cladding with substantial metal loss due to significant in-pile clad oxidation. The dominant clad failure mechanism during dry storage and the pre-storage assembly drying is therefore creep rupture. Severe embrittlement or delayed hydride cracking (as a result of the formation of radial hydrides) can also lead to clad failure, and are major concerns. The primary aim of the ENIGMA analysis is therefore to predict whether or not the AP1000 cladding could fail via these mechanisms. This is done by comparing the clad hoop stresses and clad permanent

hoop strains that are predicted during the post-irradiation operations to the primary limits of 120 MPa and 1% described in Section 2. The clad temperatures are also compared to the secondary limit of 400°C from Section 2.

A 'base case' ENIGMA analysis was performed assuming the nominal 10 year cooling time. The impact of 5 and 15 years cooling times were then explored in sensitivity studies.

During post-irradiation operations: (a) the clad creep rate was computed using the implementation of the Bouffieux model described in Appendix B; (b) the clad corrosion model was deactivated; (c) all other fuel and clad property models were unchanged from those implemented during irradiation; (d) the rod average decay heat versus time that was modelled was as calculated by the peak pin FISPIN run (see Section 3). Since decay heat is approximately proportional to burnup for cooling times of greater than a few years, the decay heat in each axial zone was set to (axial zone burnup / rod average burnup) * peak pin decay heat (as per [6.14]).

With respect to the implementation of the Bouffieux model for out-of-pile clad creep, it is noted in Appendix B that irradiation hardening effects can be deactivated. This is to simulate spent fuel cladding that has had the irradiation damage fully annealed. In order to give conservative clad creep predictions (since annealing removes the hardening effects of irradiation damage) this deactivation was invoked throughout the dry storage phase (but not during the pond cooling or assembly drying phases — despite the potential for high clad temperatures during drying, the short drying time means that any annealing is likely to be limited). This is conservative for three reasons: (a) it assumes full annealing of the irradiation damage; (b) it assumes that the annealing occurs instantaneously at the beginning of dry storage; (c) it ignores the known hardening effect of the hydrogen absorbed by the cladding during the in-pile oxidation process.

It should be noted that the Bouffieux model is strictly only applicable to Zircaloy-4. Thus, its use here for modelling ZIRLO™ material is untested. However, there is evidence from thermal creep tests on irradiated (68 GWd/tU) ZIRLO™ cladding in which dry storage conditions were simulated that the creep behaviour of ZIRLO™ in this regime is comparable to that of (cold-worked stress-relief annealed) Zircaloy-4 [6.15]. More rigorous modelling of the out-of-pile clad creep would require more information on, and potentially analysis of, the thermal creep of ZIRLO™ in assembly drying and dry storage conditions.

During spent fuel pond cooling, the clad surface temperatures were conservatively set to the AP1000 spent fuel pond water temperature design value during normal refuelling of 60°C [6.5]. The rod external pressure was set to atmospheric pressure, which is conservative with respect to clad creep (since the pressure of the surroundings would in reality include a hydrostatic pressure component). As discussed in Section 4.2, these low temperatures mean that corrosion in this environment will generally be negligible. The clad corrosion model is therefore deactivated during the pond cooling period such that no clad corrosion is modelled during the cooling.

Assembly drying was simulated with a drying period of 24 hours and an ambient temperature of 100°F, or 37.8°C — the latter is a typical value assumed in cask licensing. The 24 hour period consisted of a heat-up from spent fuel pond temperatures, a steady-state phase and a quasi-instantaneous cool-down phase to dry storage conditions. The clad heat-up rate was conservatively set to an upper limit value corresponding to the situation where the decay heat increases the internal energy of the fuel rod with no heat transfer to the surroundings. The peak clad surface temperature imposed during the steady-state phase was determined based on published data for peak clad surface temperature minus ambient temperature versus cask decay heat load per unit length, assuming drying in a transfer cask containing 24 assemblies, each with a burnup of 65 GWd/tU. The simulation of assembly drying is described in more detail in Appendix A.

During the 100 year dry storage period, an ambient temperature of 100°F was assumed, as per the assembly drying operation. The evolution of peak clad surface temperature was determined based on published data for peak clad surface temperature minus ambient temperature versus cask or silo module decay heat load per unit length, assuming dry storage in a cask containing 24 assemblies, each with a burnup of 65 GWd/tU. The resulting peak clad temperatures, and cask decay heat loads, for the 10 year cooling period, are plotted in Figure 6. The dry storage simulation is described in more detail in Appendix C.

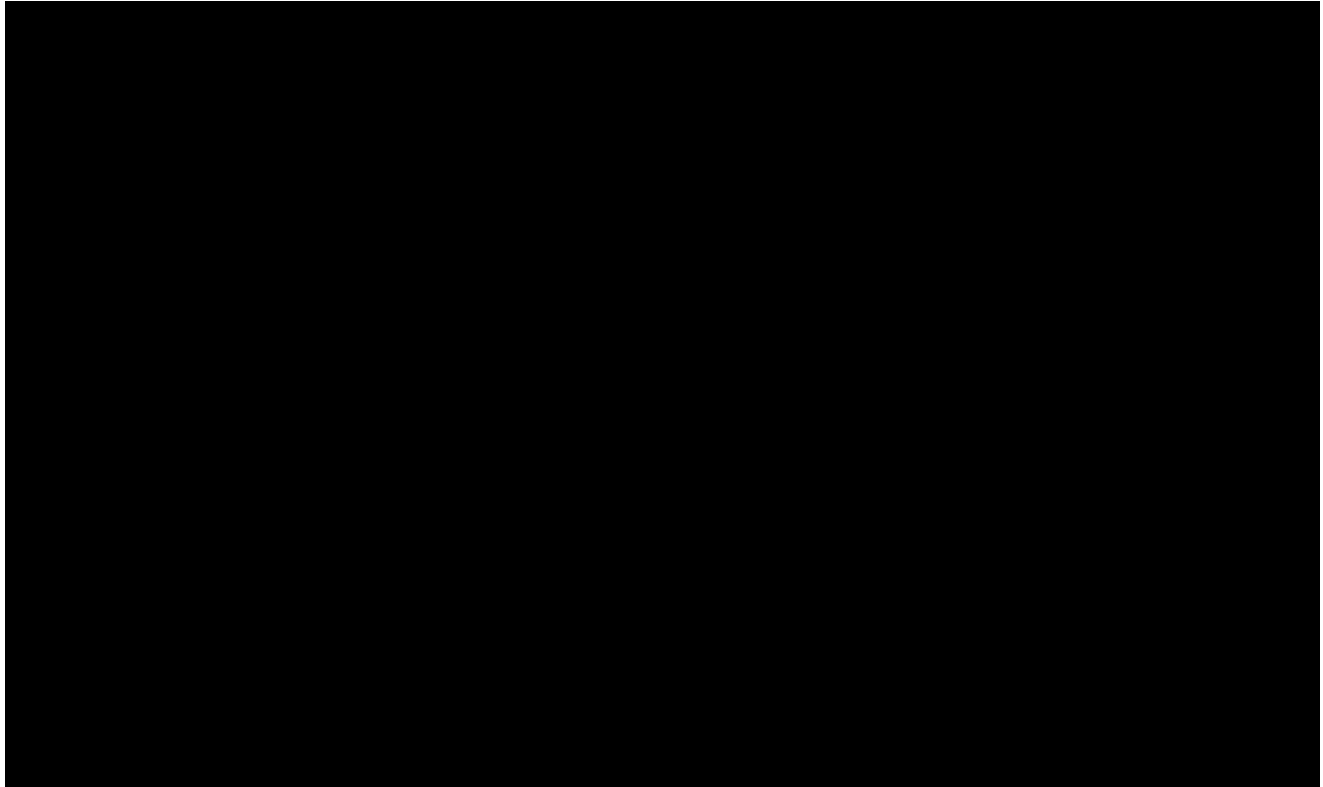


Figure 6: Peak clad surface temperature and cask decay heat load in dry storage with nominal 10 year cooling period

4.3.2. ENIGMA analysis results

No fission gas release, helium release or clad creep are predicted during pond cooling. This is as expected given the low powers (decay heat only) and clad surface temperatures relative to in-pile values. Although not modelled by ENIGMA, hydrogen diffusion in the cladding will also be negligible, and the zirconium hydride platelets formed during irradiation (by reaction of the cladding with the hydrogen produced in the clad oxidation reaction) will be stable. Hence, there is no significant impact of the pond cooling period on the cladding state.

The maximum clad hoop stresses during assembly drying and dry storage occurred in

[Redacted]

The maximum clad permanent hoop strains during assembly drying and dry storage occurred in

[Redacted]

The results during assembly drying are summarised in Table 3.

Table 3: Key ENIGMA results during assembly drying

Cooling period, years	Maximum permanent hoop strain, %	Maximum hoop stress, MPa	Peak clad temperature, °C
5	█	█	█
10	█	█	█
15	█	█	█

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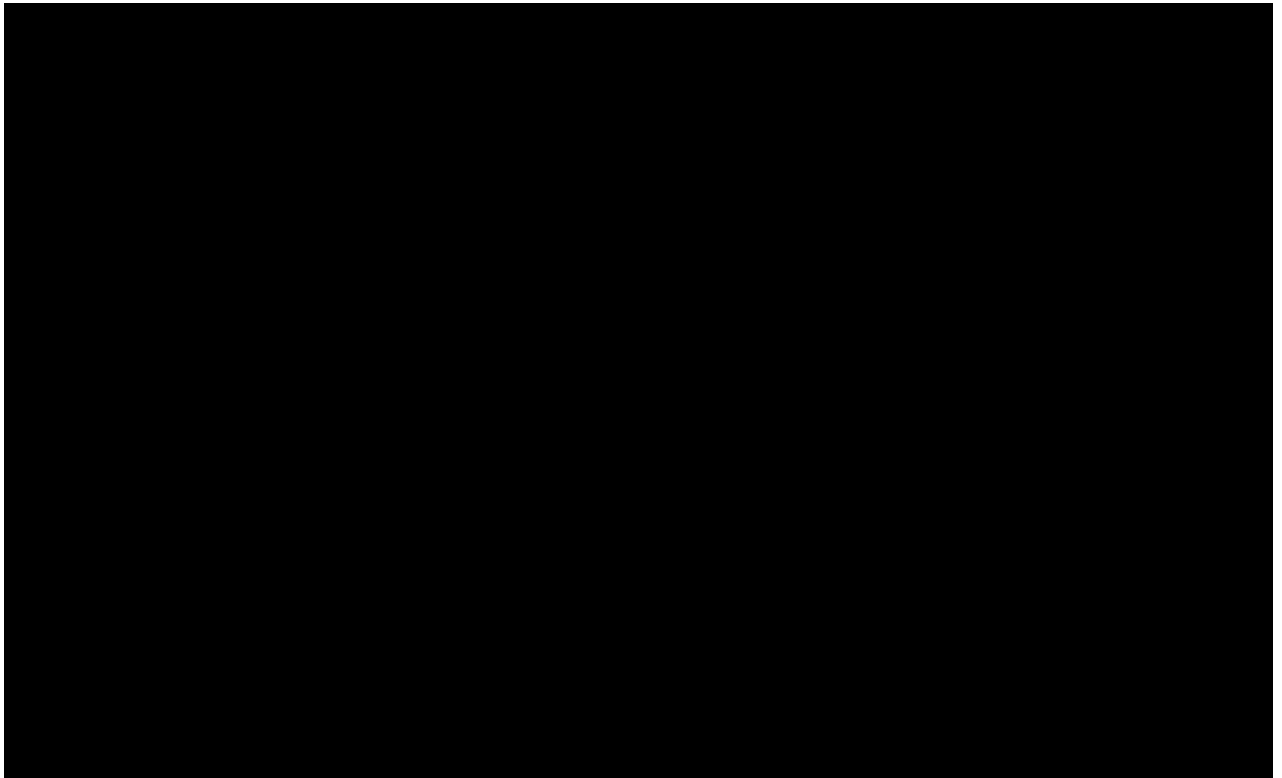


Figure 7: Clad hoop stresses in limiting axial zone during assembly drying for both standard and optimised ZIRLO™

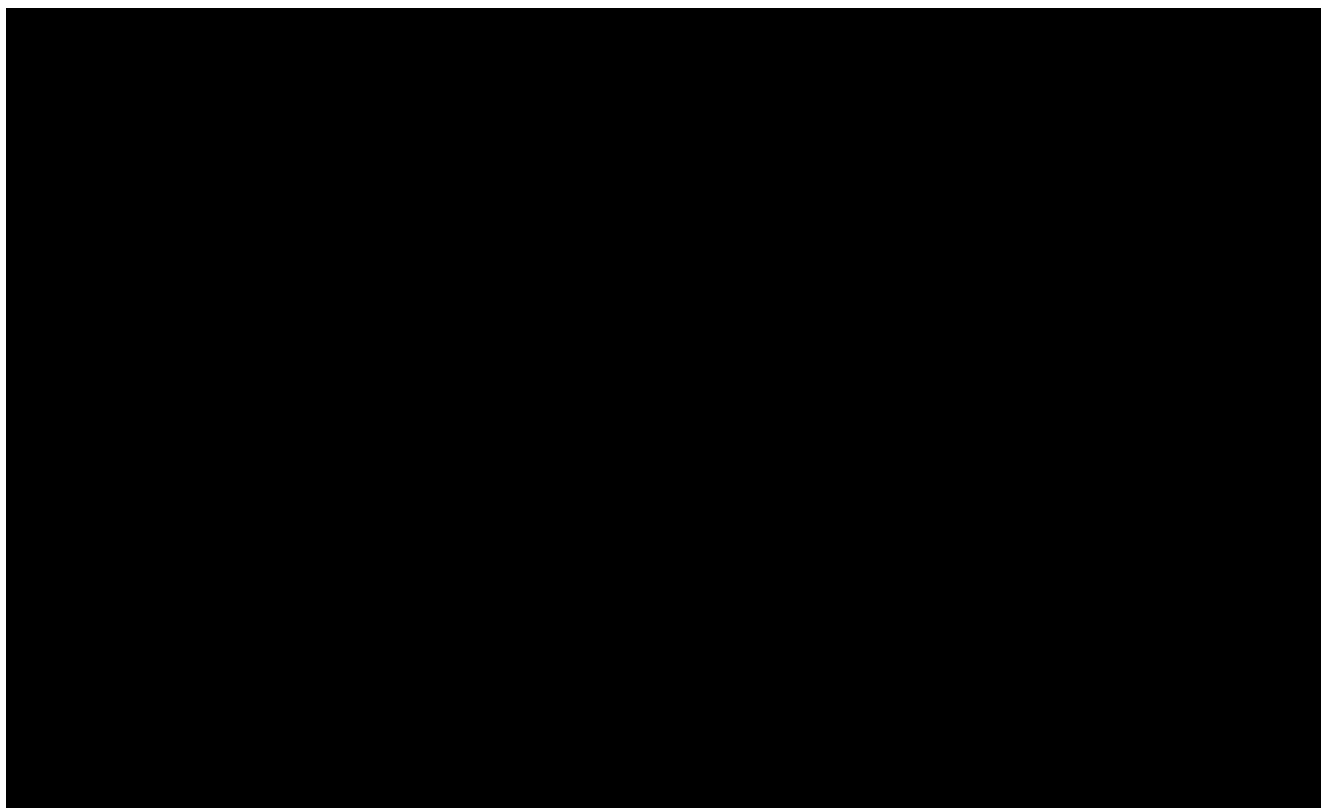


Figure 8: Clad permanent hoop strains in limiting axial zone during assembly drying for both standard and optimised ZIRLO™

The results during dry storage are summarised in Table 4.

Table 4: Key ENIGMA results during dry storage

Cooling period, years	Maximum permanent hoop strain, %	Maximum hoop stress, MPa	Peak clad temperature, °C
5	█	█	█
10	█	█	█
15	█	█	█



As an illustration of the clad strain behaviour, the clad permanent hoop strains in zone █ during dry storage are plotted in Figure 10 for the 10 and 15 year cooling times with standard ZIRLO™. █

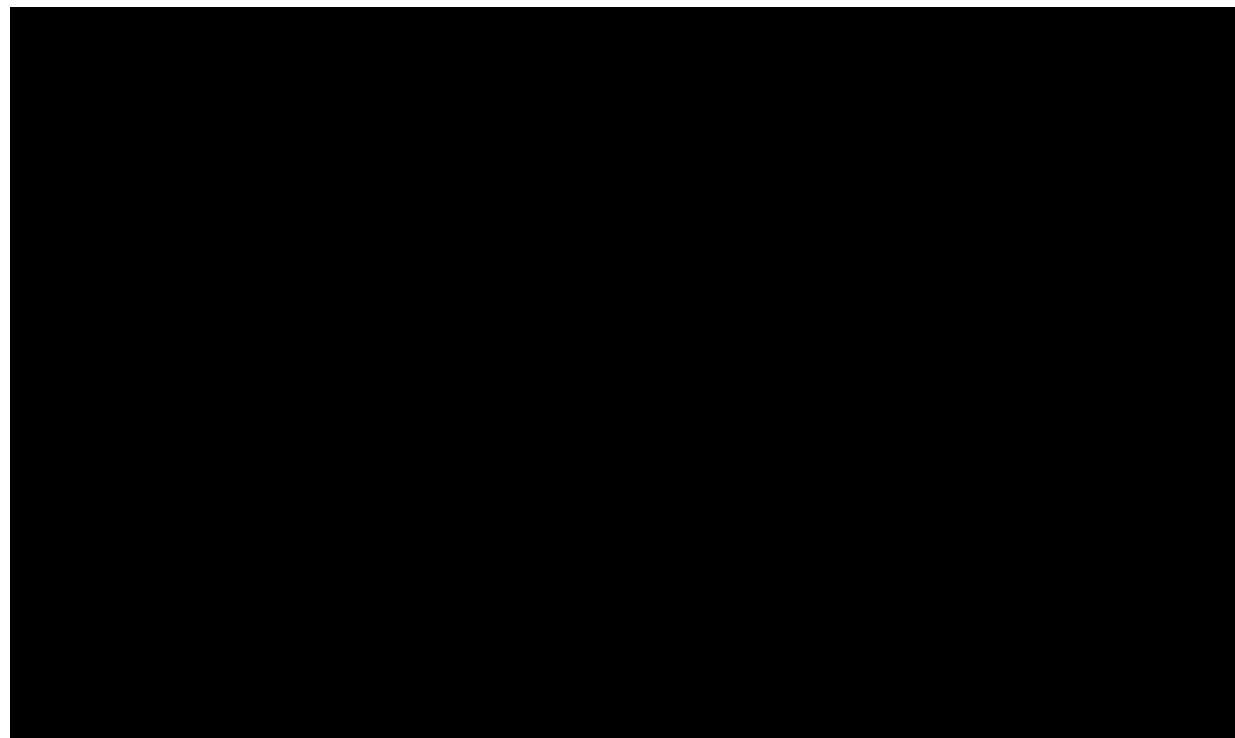


Figure 9: Clad hoop stresses in limiting axial zone during dry storage for both standard and optimised ZIRLO™

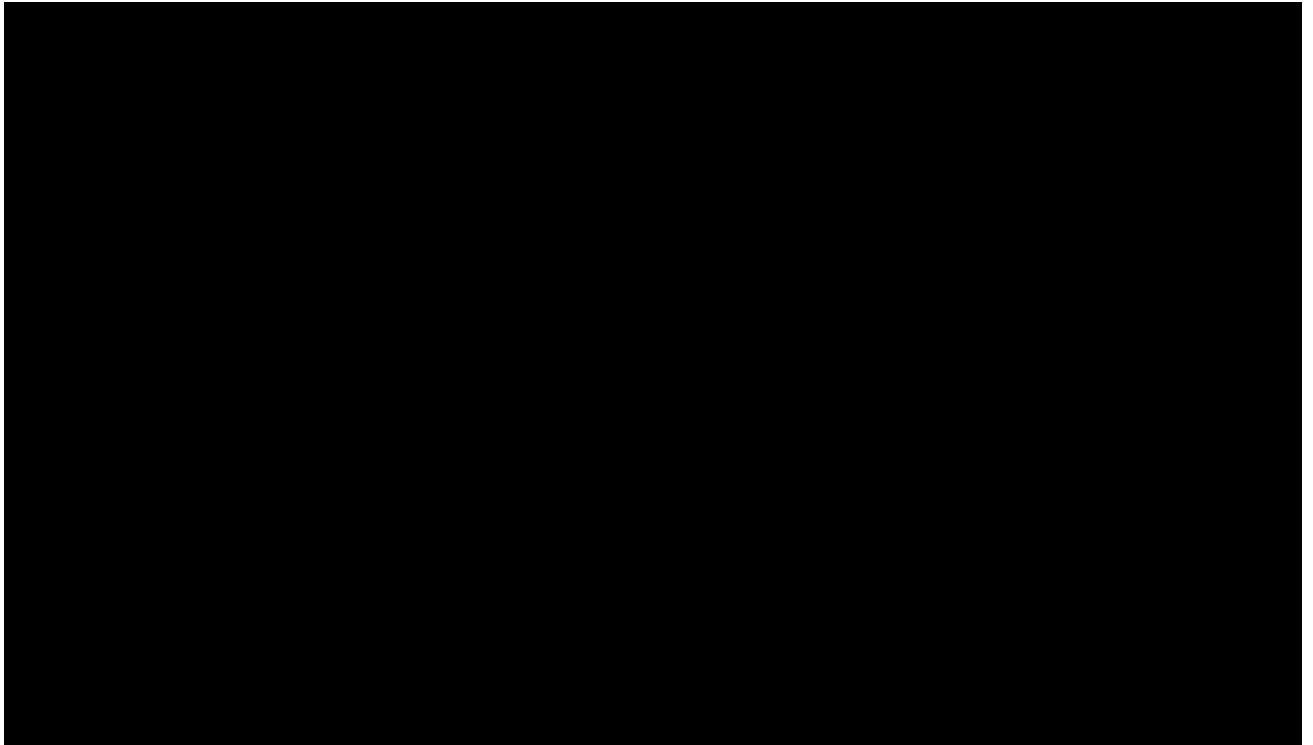


Figure 10: Clad permanent hoop strains in limiting axial zone during dry storage for 10 and 15 year cooling times and standard ZIRLO™

It should be noted that the calculations described in this section rely on many estimates, simplifications, and assumptions. It is therefore recommended that more rigorous calculations are performed, together with sensitivity studies on the key parameters, when the dry storage vault, silo or cask design is defined. The out-of-pile creep behaviour of the ZIRLO™ cladding alloy, including any annealing of irradiation damage at temperature, and any hydrogen hardening, should first be clarified. The more rigorous calculations should use results from thermal-hydraulics modelling of the chosen dry storage container design to determine the clad temperatures during assembly drying and dry storage.

Recommendation 6.2. Perform more rigorous clad stress and strain calculations for assembly drying and dry storage, together with sensitivity studies on the key parameters, when the dry storage system design is defined. The out-of-pile creep behaviour of the ZIRLO™ cladding alloy, including any annealing of irradiation damage at temperature, and any hydrogen hardening, should first be clarified.

5. Corrosion behaviour of assembly structural component materials (Task 7)

This task specifically excludes corrosion of fuel rod cladding, but, of necessity, mention has to be made of the corrosion of cladding in the context of pond storage, due to its galvanic coupling to other components.

5.1. Outline summary of AP1000 fuel assemblies

In order to assess corrosion susceptibility, a primary requirement is a materials inventory of all the components of each design of fuel assembly. From the information made available by Westinghouse, a component and materials list has therefore been compiled – see Table 5. It should be noted that it is not known how the hold-down springs are attached to the fuel assembly. It is possible that attachment screws are used, but this is not mentioned in the available information. Alongside each component is a preliminary view of its corrosion susceptibility. These considerations will be discussed in further detail in the following sections.

5.2. Corrosion mechanisms relevant to fuel assemblies in extended storage

5.2.1. Introduction

The corrosion of any metallic material is in general due to an interaction of the material itself, its condition, and its environment. Self evidently, some metallic materials are more susceptible to corrosion than others simply by the virtue of the element or alloy which comprises the metal. This susceptibility can be modified (in both directions) by the condition of the material, for example the surface finish (rough or electro-polished) or any in-built stress fields, or microstructural compositional changes from the original alloy formulation (for example radiation induced sensitisation). Finally, the environment in which the metal is placed will have a significant influence on its corrosion behaviour, by providing a benign or hostile chemical environment, or by contact with other materials with which galvanic coupling etc is possible.

In considering the corrosion of spent fuel assemblies, it will be necessary to consider all these factors in each of the principal storage environments, namely wet pond or dry vault, silo or cask storage regimes. Each of the proposed new power plant designs will as a minimum include fuel cooling ponds and the fuel must unavoidably go through these ponds as a first stage in its storage history. Therefore it is also important to recognise the imposed environment that these ponds will apply to the fuel and to recognise any consequent corrosion that could apply in this first stage of the storage history. It is not the remit of this present work to consider corrosion in station ponds; however any corrosion experienced there will influence the starting condition of materials placed in longer term storage. Therefore it is important to at least recognise what these pond environments will be, in terms of chemistry, contact with other materials, and other factors. The available information is summarised in Table 6.

Table 5: AP1000 fuel assembly components

Fuel Assembly Component	Material	No. in One Assembly	Dimensions (mm)	Corrosion Susceptibility	References
Top nozzle	AISI 304	1	[REDACTED]	Low	EPS-GW-GL-700 Sec 4.2
Top grid (body)	Alloy 718	1		Can be susceptible to IGSCC	EPS-GW-GL-700 Sec 4.2
Holddown leaf springs	Alloy 718	4		Can be susceptible to IGSCC	EPS-GW-GL-700 Sec 4.2
Bottom grid (body)	Alloy 718	1		Can be susceptible to IGSCC	EPS-GW-GL-700 Sec 4.2
Protective grid plate in FA bottom nozzle	Alloy 718	1		Can be susceptible to IGSCC	EPS-GW-GL-700 Sec 4.1
Protective grid plate spacers	Alloy 718	4	[REDACTED]	Can be susceptible to IGSCC	EPS-GW-GL-700 Sec 4.2
Bottom nozzle	AISI 304	1	[REDACTED]	Low	EPS-GW-GL-700 Sec 4.2
Bottom nozzle thimble screws	Unknown	24		Unknown	EPS-GW-GL-700 Sec 4.2
Thimble screw locking cup	Unknown	24		Unknown	EPS-GW-GL-700 Sec 4.2
Control rod guide thimbles	ZIRLO™ or Zr-4	24	[REDACTED]	Low unless hydrided	EPS-GW-GL-700 Sec 4.2 & Sec 4.3
Guide thimble assembly	Unknown	24		Unknown	EPS-GW-GL-700 Sec 4.2
Guide thimble bottom dashpot assembly	ZIRLO™ or Zr-4	24	[REDACTED]	Low unless hydrided	EPS-GW-GL-700 Sec 4.2
Guide thimble top lock tube	AISI 304	24		Low	EPS-GW-GL-700 Sec 4.2
Intermediate grids	ZIRLO™	8	[REDACTED]	Low unless hydrided	EPS-GW-GL-700 Sec 4.2
Intermediate flow mixer grids	ZIRLO™	4	[REDACTED]	Low unless hydrided	EPS-GW-GL-700 Sec 4.2
Grids (straps)	ZIRLO™ or Zr-4	Components of grids	[REDACTED]	Low unless hydrided	EPS-GW-GL-700 Sec 4.2
Grids (springs)	ZIRLO™ or Zr-4	Components of grids	[REDACTED]	Low unless hydrided	EPS-GW-GL-700 Sec 4.2
Fuel rod cladding	ZIRLO™	264	[REDACTED]	Low unless hydrided	EPS-GW-GL-700 Sec 4.1
Fuel rod end-plugs	ZIRLO™?	528		Low unless hydrided	EPS-GW-GL-700 Sec 4.2
Instrumentation / supporting tube	ZIRLO™ or Zr-4	1	[REDACTED]	Low unless hydrided	EPS-GW-GL-700 Sec 4.2

Table 6: AP1000 fuel pond environment

Storage System Component	Material	Number or Value	Corrosion Susceptibility	References
Spent fuel assembly (SFA) channels	N/A	884		EPS-GW-GL-700 Sec 9.1
Region 1 SFA channels	N/A	243		EPS-GW-GL-700 Sec 9.1
Region 2 SFA channels	N/A	641		EPS-GW-GL-700 Sec 9.1
Defective SFA channels	N/A	5		EPS-GW-GL-700 Sec 9.1
Material of construction	Metamic encased in stainless steel	N/A	Of concern if not fully encased	EPS-GW-GL-700 Sec 9.1 EPRI report 1003137
Storage timescale	N/A	Assumed up to 15 years		EPS-GW-GL-700 Sec 9.1
Radiation dose rate	Primarily gamma	Unknown		EPS-GW-GL-700 Sec 9.1
Water chemistry — pH	LiOH	"Slightly acidic"		EPS-GW-GL-700 Sec 9.1
Water chemistry — boric acid	H ₃ BO ₃	2700 ppm B		EPS-GW-GL-700 Sec 9.1
Water temperature — normal operations	N/A	60°C		EPS-GW-GL-700 Sec 9.1
Water temperature — limiting	N/A	93°C		EPS-GW-GL-700 Sec 9.1
Pool liners	Stainless steel	Whole pool	Low	EPS-GW-GL-700 Sec 9.1

5.2.2. Zirconium alloy general corrosion

Zirconium alloys are the major structural materials employed within the fuelled regions of all water-cooled nuclear power reactors. The majority of zirconium corrosion data relates to reactor operating conditions. The corrosion of zirconium in water follows the equation



Recent corrosion data obtained under conditions of high heat flux are unlikely to be amenable to extrapolation to pond storage temperatures. Early corrosion data was however obtained from non-heat transfer specimens in in-reactor loops and, in principle, could be extrapolated to pond storage temperatures. Values for the activation energy of the oxidation reaction are spread over the range 30 to 51 kcal/mole [7.1], with no clear agreement over the nine studies reporting those results. If an Arrhenius type relationship is assumed then at pond storage temps corrosion rates could be a factor of 10^{10} lower than those obtained in-reactor [7.2]. In-reactor corrosion rates are dependent on numerous factors such as alloy composition, fabrication procedure, heat flux through the cladding and its evolution with time as a result of the use of burnable poisons, water temperature, the thermal hydraulics of the fuel assembly design and the water chemistry [7.3]. Generally end of in-reactor life is determined by the onset of oxide spalling which generally occurs when the film is ~100 microns thick.

The mechanism for zirconium alloy corrosion is that once an oxide layer is formed, it maintains a thin, intact and highly protective layer close to the surface. Due to the change in density of the oxide (compared with the metal) the oxide has a larger volume than the metal and expands outward but in so doing it is prone to crack and outer parts of the oxide will spall off. The inner, protective layer is maintained. Oxide growth is by inward migration of oxidising species to the metal / oxide interface, through the inner oxide layer. The decomposition of water to produce these oxidising species is thought to take place at lattice defect sites within the oxide so that oxide vacancies are filled, and oxide ions diffuse inwards to react with the metal; also the hydrogen formed by the process diffuses inwards and is partly soluble in the zirconium alloy metal.

In-reactor corrosion kinetics are usually derived from weight gain measurements assuming that all the oxide formed remains on the specimen and converted to an oxide thickness (assumed to be uniform) using the theoretical density of ZrO_2 . Also experimental results need to be corrected for the amount of hydrogen absorbed. The weight gain kinetics for zirconium alloys usually fall into two periods referred to as pre- and post-transition. The initial, pre-transition period is characterised by a decreasing rate of weight gain usually following a cubic or quartic growth kinetic curve rather than the parabolic kinetics predicted from a theoretical consideration of the corrosion mechanisms occurring. The oxide forms under compression because of its larger volume compared to the volume of metal from which it is formed. When the oxide thickness reaches about 2 microns, the oxidation process increases to a post-transition (approximately linear) rate. The transition is indicative of the generation of porosity in the previously impervious oxide film [7.4].

Lithium hydroxide is added in PWR reactors to render the coolant slightly alkaline in order to inhibit deposition of corrosion products on the fuel cladding. The corrosion rate of zirconium alloys is increased at high pH [7.5-7.7] due to the earlier formation of porous oxide films. At very high lithium concentrations the pre-transition kinetic period disappears. At lower lithium concentrations approximately cubic pre-transition kinetics are exhibited with little evidence of an enhanced corrosion rate but with reduced times to transition. In corrosion experiments specimens exhibit lower weight gains in alkaline solutions (both LiOH and NaOH) which are taken as evidence for dissolution of the oxide film [7.8]. This is not unexpected, as ZrO_2 is amphoteric [7.3].

5.2.3. Zirconium hydride formation

The most significant risk of corrosion in stored PWR fuel relates to delayed hydride cracking of zirconium and its alloys. In a sense it is corrosion, with a hydride compound as the corrosion product.

The mechanism for DHC is that the hydrogen formed by corrosion of Zr to give ZrO_2 goes into the metal and there exists as a solute within the metal phase. It will react with Zr when it exceeds the solubility limit for the conditions which apply. Hydrogen has very limited solubility in zirconium alloys, less than 1 ppm at ambient temperature and about 80 ppm at 300°C. When the solubility limit is exceeded zirconium hydride precipitates and as this phase is brittle it can adversely affect the mechanical properties and in some instances (Hanford N Reactor fuel assemblies) mechanical handling has led to cladding damage [7.9]. At the end of irradiation cladding can contain between 250 – 600 ppm hydrogen, most of which will be present as the hydride since it is in excess of its solubility limit. Because the cladding has operated under heat flux the temperature gradient concentrates the hydrides in the outer layers of the cladding precipitating predominantly just beneath the outer diameter in a series of platelets which jointly appear as clusters forming a circumferential rim. The individual platelets are oriented radially (with some scatter), since these have formed in either intergranular locations or crystal planes orthogonal to the applied stress which is (for a tube) parallel to the outer surface.

As the fuel cools, the solubility of hydrogen in zirconium becomes lower and slightly more hydride will precipitate. At cooling pond temperatures, the hydrides are frozen in.

The real concern is that during extended storage the hydride platelets may grow or re-orientate to give radially-oriented hydrides which provide intergranular paths of weakness through the walls of the guide thimbles and the fuel cladding. The probability of cracking depends on the angular distribution of re-oriented hydride platelets, their size, and their extension by further hydriding (zirconium alloys respond to stresses by combining with hydrogen which is in solution within the metal itself). There are several other variables such as temperature, hydrogen concentration, and stress intensity, which will all have a bearing on the rate and extent of hydride cracking. It is not within the scope of this study to perform the complex calculations that would be necessary to evaluate the propagation of delayed hydride cracking, but its importance should be noted.

The zirconium hydride is not a problem in pond stored fuel as the platelets remain disconnected from each other. However, for dry stored fuel during the drying process, fuel temperatures as high as 400°C may be reached, and under these conditions the hydride will partially re-dissolve so the hydrogen is in equilibrium with its solubility level at that temperature. If the fuel is again cooled (in a way enabled by drying cycles comprising vacuum drying then a flow of warm gas) then the hydrogen will again exceed its solubility limit and will precipitate once again. This may involve some re-orientation, particularly if stress fields are different and are aligned more radially. On the other hand, there is some memory effect: where a hydride platelet has partly re-dissolved there will be a void which may be an easier route for new hydride to re-precipitate, so complete re-orientation is unlikely.

An additional factor is that reactor neutron fluxes generally harden metals (i.e. increase their strength and decrease their ductility). For high burnup assemblies the decrease in ductility may be sufficient to markedly reduce low temperature impact strength [7.9]. For zirconium alloys, the radiation induced loss of ductility is exacerbated by the formation of hydride platelets which present locations of weakness and embrittlement. Provided sufficient care is taken when handling fuel reduced cladding ductility has not impacted on the ability to handle fuel after periods of pond storage. The same effects are expected to occur in zirconium alloy structural components of fuel assemblies.

Studies at Westinghouse, Battelle and elsewhere have revealed that the nickel in Zircaloy-2 was responsible for the hydrogen pickup. This has led to the development of Zircaloy-4, which has significantly less nickel than Zircaloy-2 and is less susceptible to embrittlement. In addition, the introduction of niobium into Zircaloy-4 further reduces the amount of hydrogen absorption. Metallurgical examination did not find any evidence for increased hydrogen content or changes in hydride distribution after 20 years storage of Shippingport Zircaloy clad fuel [7.10]. Delayed hydrogen cracking is a mechanism that has caused degradation of zirconium alloys at relatively low temperatures but at pond storage temperatures this mechanism does not appear to be operating [7.11].

A contributory factor to hydride cracking is the incidence of a stress field, present during the storage period. A number of possible features could raise a stress field, particularly notches or cracks. A possible cause of stress is the consequence of metal thinning during irradiation due to the onset of fretting wear, which is the mechanical abrasion of the grids and springs against the fuel pins and control rod guide tubes as a result of a flow-induced vibration. Most often this has been considered with a view to pin failure, but the same mechanism can apply to the guide tubes. It is not necessarily that the abrasion itself cuts through the metal of the pin cladding or guide tube, but that the abrasion removes the protective surface oxide, exposing fresh metal, which immediately oxidises to give a fresh oxide layer, which in turn is abraded away. Thus an accelerated form of corrosion is possible. This mechanism has been well known for many years, and various means of quantifying it and mitigating it have been explored. More recently, however, it has been recognised [7.12] that a thinning (but not failure) of a zirconium alloy tube will nevertheless influence the stress fields associated with that component, which in turn may affect its susceptibility to delayed hydride cracking. Fretting wear is addressed in WCAP-12610 [6.7] and allowance for it is considered to be within the design basis of the fuel (see also Section 4.1).

5.2.4. Zirconium alloy stress / creep

Zirconium alloy structural components are not expected to demonstrate stress or creep in pond storage. This is by analogy with known characteristics of fuel cladding: internal cladding pressure is relatively low at pond storage temperatures and cladding creep is negligible [7.13, 7.14]. In addition, stress dependant thermally activated cladding degradation mechanisms are practically frozen at typical pond storage temperatures of around 40°C [7.13]. The stress experienced by zirconium alloy components will not change during storage (unless MOX fuel is used) and in pond storage the temperature is too low for the metal to creep (normally requiring a temperature of at least half the melting point for thermal creep to become evident).

5.2.5. Stainless steel and Inconel general corrosion

Austenitic stainless steels and Inconel alloys are notably resistant to uniform corrosion having operated at LWR reactor temperatures. Under pond storage conditions corrosion rates for stainless steels and Inconel alloys are difficult to measure. Korean data reported to BEFAST III CRP found corrosion rates of stainless steel in ponds to be 0.01 – 0.1 microns per year regardless of the stainless steel type and pre-treatment histories [7.13]. Results from stainless steel coupons exposed to (untreated) pond water indicated uniform corrosion of [REDACTED] microns per year [7.15]. The effect of hydroxide ions as a corrosion inhibitor for stainless steels is not widely reported in the open literature, but it has been observed to influence polarization measurements [7.16] as an inhibitor of pitting corrosion in chloride solutions.

It should also be noted that in an irradiated environment, stainless steel also experiences attack by oxidising radicals formed by the radiolysis of water. (In this regard simple corrosion testing in pond water chemistry is not fully adequate.) In the early 1980s a significant programme of work was carried out by UKAEA to investigate the storage of FA materials during extended transport and storage, including the effects of water radiolysis. The primary aim of that work was gas generation, in sealed bottles or flasks (which would be relevant to any pond stored fuel which has been segregated for reasons such as pin failure). However, corrosion of materials was observed and reported [7.17]. The corrosion products of stainless steel were often observed to be colloidal species. The amount of corrosion was slight, and not a reason to expect any structural failure.

The general corrosion rate of Inconel would be expected to be similar to, or lower than, that of stainless steel. Inconel was first developed as an alloy for use in the food processing industry, having a high resistance to chloride-induced pitting attack. Consequently it was adopted by the US Navy for use in submarine reactors as steam generator tubing, and thus by the civil power industry.

The Inconel components of fuel assemblies are expected to be slightly oxidised after reactor operation. A very thin oxide layer, comprising a nickel / iron / chromium spinel is expected. There is extensive experience of Inconel corrosion under primary circuit chemistry conditions. The propagation of a corrosion front, and the kinetics of that process, have been extensively studied and reported, see for example [7.18]. This will of course affect the condition of any Inconel components at the point of discharge from reactor.

At pond temperatures, general corrosion rates will be much lower (and essentially negligible).

Also reported in [7.18] is a pH-dependence of Inconel general corrosion (again at operating temperature) across the range 6 to 8. The trend is towards lower corrosion rates at higher pH. There is no reason to suppose a qualitatively similar trend will not apply at pond temperatures. Therefore, storage in a pond with a managed pH above neutral should be beneficial in terms of minimised general corrosion.

5.2.6. Inter-granular stress corrosion cracking (IGSCC) of stainless steel

The basis of this mechanism is that a combination of material condition, stress and environment combine to interact in a way which results in intergranular stress corrosion cracking.

However, this mechanism has a number of pre-requisites.

1. The stainless steel is in a sensitised condition. Stainless steels are susceptible to sensitisation, a mechanism that causes depletion of chromium levels adjacent to grain boundaries leaving the material vulnerable to intergranular attack when exposed to even low levels of aggressive species. Sensitisation can occur by thermal or irradiation mechanisms both of which leave grain boundary regions denuded in chromium. Thermal sensitisation involves the diffusion of chromium away from grain boundaries, it precipitates as chromium carbides leaving a grain boundary depleted in chromium; thermal sensitisation, e.g. by welding, is possible, but more prevalent in high-carbon steels where the chromium carbides are favoured. Radiation induced sensitisation involves the action of fast neutrons displacing chromium atoms from their lattice sites near the grain boundaries, coupled with preferential diffusion of chromium away from grain boundaries to fill radiation-induced vacancies in the metal matrix. The irradiation must be to an appropriate fast neutron flux to displace adequate chromium atoms. Also, the irradiation must take place within a defined temperature range (350 to 520°C)

with a peak susceptibility at around 380 to 440°C, which enhances the mobility of chromium atoms displaced by irradiation. In the present context, it is not credible that any stainless steel component of a PWR fuel assembly will reach the peak temperature when under irradiation. The hottest component (Zircaloy fuel cladding) will have experienced temperatures of only possibly 360°C. The stainless steel top nozzle components will experience at least the outlet water temperature (330°C) and possibly slightly higher if there is some thermal conductivity through the structure of the fuel assembly. Also the neutron spectrum and flux will be different to that in AGRs where this is a definite known problem [7.19]. It may be necessary to express a note of caution if PWR fuel is loaded in a high duty core where stainless steel component temperatures may just begin to enter the range where sensitisation can apply.

2. In stainless steels, stress is a requirement to intergranular stress corrosion cracking. This may come from a range of sources, such as hoop stresses at manufacture, residual cold work stresses, welding stresses and thermal stresses, having been temperature cycled whilst coupled to a different metal. The top nozzle of a fuel assembly is a comparatively large component, but it is not evident that it will carry any residual stresses due to manufacture (bends or welds). There may be some stress at the interface with the zirconium alloy guide thimbles, if differential expansion or radiation-induced creep has caused the zirconium alloy tube to seek to expand, at the same time as expansion of the stainless steel nozzle component has caused the hole for the guide tube to shrink. The incidence and magnitude of stresses within the top nozzle requires careful assessment which lies outside the scope of this study; the point is made here that stresses may exist, facilitating IGSCC.
3. There must be an aqueous electrolyte to support corrosion propagation within the growing crack. In a pond the source of water is evident. In a dry store it will depend on the effectiveness of drying and on the temperature of the component (i.e. whether water will have vaporised from the surface).

By virtue of the irradiation temperature being (at worst) only borderline for the initiation of RIS, the required sensitisation condition is unlikely. The required stress field may exist. The required aqueous phase will exist in ponds, but is unlikely in dry stores. The top nozzle components are comparatively large and have a thickness of about ■■■ mm. Therefore cracking through a top nozzle is very unlikely, but cannot be totally excluded in a pond context.

Recommendation 7.1. Perform calculations to definitively establish the maximum temperature and fast neutron dose of the stainless steel top nozzle during irradiation, and assess its susceptibility to radiation induced sensitisation.

5.2.7. Localised corrosion of Inconel alloys

Inter granular stress corrosion cracking of Inconel alloys exposed to PWR primary circuit chemistry has occurred almost exclusively in alloys 600 and X750. To a much lower extent, it has been observed in weld metal alloys 182 and 82. The alloys used in AP1000 fuel assemblies are not recorded as subject to localised corrosion.

5.3. Review of extended pond storage of PWR fuel

The currently available long-term pond storage capability for PWR fuel would primarily be the current THORP receipt and storage pond at Sellafield.

The Thorp R&S pond currently operates with a demineralised water purge. Both AGR and LWR fuels are present in the pond but AGR fuels are in closed containers with their own high-pH chemistry because of their susceptibility to corrosion of sensitised components at neutral pH. LWR fuels are stored in Multi-Element Bottles (MEBs) which contain aluminium components, these would corrode at high pH which is why the pond as a whole cannot be operated at high pH. If this pond were to be used for the long-term storage of AGR and PWR fuels, then assuming the MEB materials issue is dealt with it would be desirable to store the AGR fuel in the open pond. That would still require the use of a suitable corrosion inhibitor, such as sodium hydroxide to give a pond water pH of at least [redacted] or sodium nitrate to give a nitrate concentration of at least [redacted] ppm.

Those pond chemistry requirements for AGR fuel are distinctly different to those employed at power station ponds for the immediate storage of spent PWR fuel on discharge from reactor.

It is considered likely that extended storage times of 80 to 100 years may be required. This review identifies any potential degradation mechanisms which may operate to prevent the safe storage of this fuel over the timescale required.

5.3.1. Source data available

The BNFL Post Storage Examination programme for LWR fuel assemblies was limited to infrequent underwater visual inspection. This was considered to be adequate as pond storage times were expected to be short as the fuel was scheduled for reprocessing. This type of examination is incapable of providing quantitative data on the extent of any corrosion occurring.

There have been numerous IAEA co-ordinated research projects (CRP) which considered extended storage of spent nuclear fuel and the reports produced are in the public domain [7.2, 7.4, 7.9, 7.13, 7.14, 7.20, 7.21, 7.22]. There has been UK participation in some of these programmes but this has generally been associated with the long-term storage of AGR fuel. A general trend in these CRP's is that increasing storage times of spent fuel need to be considered and that most countries' response to this is to consider dry storage options. There are two notable exceptions. In Sweden the underground storage pond facility, CLAB, is expected to have an operational lifetime of at least 65 years [7.2]. In Switzerland an advanced storage pond, with passive cooling, is planned for extended storage including MOX fuel [7.23].

5.3.2. Degradation mechanisms operating during pond storage

Specific issues of fuel assembly corrosion under pond storage conditions are now considered. These supplement the more generic corrosion mechanisms discussed in Section 5.2.

5.3.2.1. Zirconium alloy general corrosion in pond storage

Quantitative zirconium corrosion data relevant to fuel storage ponds is, compared to the above, very limited. BEFAST III CRP [7.13] concluded that with (then) existing pond storage times of over 30 years the data indicated cladding corrosion rates to be extremely low (virtually not measurable) and did not limit storage times below 100 years. The condition of CANDU fuel has been characterised and then re-examined after 27 years pond storage which showed no measurable corrosion of the cladding had occurred [7.24]. No evidence of degradation of Zircaloy clad corrosion after 27 years in up to 760 ppm chloride (from biocide treatments) was observed in video inspections [7.25]. Some attempts at measuring zirconium corrosion rates during pond storage have been made using corrosion coupons. Weight measurements indicated a corrosion rate of less than [REDACTED] microns per year [7.15]. The absence of detectable interference colours on the Zircaloy coupons suggested a corrosion rate of less than [REDACTED] microns per year [7.15]. Extrapolation of corrosion data from higher temperatures to 100°C indicated oxide growth of [REDACTED] microns in 100 years [7.26]. Weight loss measurements of Zircaloy-2 coupons exposed for 3 years to demineralised water in a spent fuel storage pond gave corrosion rates of 6×10^{-4} to 6×10^{-3} microns per year [7.27]. An even lower corrosion rate, of 1×10^{-6} microns per year, has been quoted derived from 40 years operational experience of fuel storage [7.2].

Experience of pond storage of zirconium clad fuel in caustic or nitrate dosed ponds is nonexistent. Generally zirconium and zirconium alloys are considered to have good resistance to caustic solutions although this judgement is being made in the context of chemical plant corrosion not spent nuclear fuel storage. A 1981 paper has been found [7.28] which, in a table, summarises zirconium alloy corrosion data in various caustic solutions. This table is also reproduced in a 2000 publication [7.3], which suggests that little new corrosion data have been produced. The concentration of the caustic solutions and the temperatures generally far exceed those expected to occur during pond storage. Corrosion rates listed include [REDACTED] microns per year for 5% NaOH solution at 21°C, [REDACTED] microns per year in 50% NaOH at 38°C and [REDACTED] microns per year in 10% NaOH and 15% NaCl at 82°C. Corrosion data produced by Teledyne Wah Chang Albany laboratory are quoted for 50% NaOH at 30°C as [REDACTED] microns per year [7.28]. Given the highly concentrated nature of the solutions for which corrosion data are available, the minimum value of [REDACTED] microns per year is tentatively taken as a maximum value for zirconium alloy corrosion in the considerably more dilute caustic pond water.

Comprehensive sources of corrosion data [7.29, 7.30] have been searched but do not include any information for zirconium in sodium nitrate solutions (and if they did would only give the corrosion rate as less than 25 – 50 microns per year, this being a consequence of corrosion rates being quoted in bands). Mechanistically, there is no obvious reason to expect nitrate ions to have an effect on the corrosion of zirconium alloys.

Recommendation 7.2. Further data should be obtained or commissioned on corrosion of zirconium alloys in pond storage conditions. In particular, data on caustic or nitrate dosed pond water should be sought.

5.3.2.2. Zirconium alloy localised corrosion in pond storage

[REDACTED]

5.3.3. Discussion of PWR fuel corrosion experience during extended pond storage

The very low corrosion rates identified for Zircaloy and stainless steel mean that general corrosion offers no threat to the integrity of fuel pins or fuel assembly components over the storage time required. Data on zirconium corrosion in caustic solutions are limited. The inferred maximum corrosion rate in caustic pond water of [REDACTED] microns per year (see Section 5.3.2.1) implies [REDACTED] microns metal loss during 100 years storage. No data on zirconium corrosion in nitrate solutions could be found but it is considered likely that the corrosion rate remains that expected in demineralised water. It should be possible to confirm that low Zircaloy corrosion rates exist in caustic and nitrate solutions over short timescales (~ 1 month) using high resolution corrosion probes.

The general corrosion of stainless steel and Inconel components will be negligibly low in a storage pond context. The extent of general corrosion on discharge from the reactor will effectively be frozen when the fuel is cooled to storage pond temperatures, at the reactor and will remain so in extended pond storage. The available data indicates maximum corrosion rates for stainless steel of the order [REDACTED] microns per year, which is a trivial amount in the context of the dimensions of the top nozzle etc, as indicated in Table 5.

The only forms of localised corrosion that have been observed during the pond storage of LWR fuel are inter-granular attack or inter-granular stress corrosion cracking, but that is no longer considered to be a threat as materials and techniques have evolved to eliminate thermal sensitisation. No evidence for irradiation assisted stress corrosion cracking of stainless steel components in LWR fuel has been found at Sellafield. (Note: no top nozzles have been subjected to metallurgical examination, and it is borderline whether stainless steel components of PWR fuel would be radiation-sensitised at all). As the degree of sensitisation in AGR fuel is greater any storage regime that preserves AGR fuel pin integrity will prevent inter-granular attack occurring in PWR fuel assemblies. The introduction of inhibitors to prevent corrosion of AGR fuel would be equally effective in preventing corrosion of the stainless steel and Inconel components of PWR fuel assemblies.

5.3.4. Summary of PWR fuel corrosion during extended pond storage

- Reported general corrosion rates of Zircaloy and stainless steel are very low and should pose no threat to fuel integrity over a 100 year storage time. For Zircaloy, the highest corrosion rate identified under pond conditions, [REDACTED] microns per year, implies [REDACTED] microns metal loss during 100 years storage. For stainless steel, the highest corrosion rate is [REDACTED] microns per year, which implies about [REDACTED] microns metal loss during 100 years storage. Both these amounts of metal loss are negligible in the context of the component dimensions for AP1000 fuel.
- Inconel components are not structural and their general corrosion will also have a very low rate under pond conditions.
- Inter-granular attack of stainless steels due to thermal sensitisation can be dismissed due to the advances in fuel materials and fabrication techniques. The possibility of radiation induced sensitisation (RIS) cannot be fully excluded as irradiation temperatures may be close to those required for the onset of RIS. Fuel assembly component temperature details under irradiation need to be checked to eliminate the possibility of radiation induced sensitisation. As the degree of sensitisation in AGR fuel will be greater, any storage regime that preserves AGR fuel pin integrity will also prevent inter-granular attack occurring in PWR assemblies.

- No change in clad ductility is expected to occur at pond storage temperatures.
- Corrosion rate data for Zircaloy in caustic solutions are limited. The inferred maximum corrosion rate in caustic pond water of [REDACTED] microns per year implies [REDACTED] microns metal loss during 100 years storage.
- No corrosion rate data for Zircaloy in nitrate solutions have been found. However, it would be reasonable to assume that corrosion rates are unchanged from those in demineralised water.

5.4. Extended dry storage of PWR fuel

5.4.1. Initial condition of dry stored fuel

The initial condition of PWR fuel, prior to any extended dry storage, will be that it has been irradiated, discharged from reactor, pond stored at the power station site for probably a minimum of ten years (and quite possibly up to [REDACTED] years). Therefore the fuel will have thermally cooled, and its radioactivity will have decreased in line with relevant half-lives. On emplacement in a dry store, with a reduced ability to conduct heat away from the fuel, the fuel temperature will increase again and that will have a number of consequences.

The incidence of zirconium hydrides in the fuel cladding (and other zirconium components of the fuel assembly) will have stabilised during pond cooling to include the possibilities of peripheral hydrides around the outer diameter and metal / air interface, along with laminar platelets which were originally randomly oriented, but with time tend to align in response to mechanical and thermal stresses located throughout the metal.

Removing the fuel from a pond into a gas environment will have the effect of losing the good thermal transfer characteristics of the surrounding water. Increasing the temperature will have the effect of re-ordering the zirconium hydride platelets [7.34] such that they can re-align differently and potentially in a manner more susceptible to hydride cracking.

After pond storage over the order of ten to twenty years at the reactor station, the fuel is expected to have experienced minimal aqueous corrosion, as outlined above.

5.4.2. Gas phase environment

In a dry store, the fuel is invariably in contact with a cover gas (the only alternative is a vacuum system, which has never been deployed). The gas may be air, or an inert gas such as helium or argon. Both types of gas environments have been deployed. However, in practice it is not normally possible to completely exclude all traces of air and water vapour, so to some extent, the cover gas will include a proportion of air and water vapour.

The cover gas will unavoidably be irradiated, by the decay radiation emanating from the fuel and its associated (activated) assembly components. The cover gas will interact with the radiation and will undergo radiolysis. The usual products are oxides of nitrogen, and nitric acid vapour. In the case of air, the formation of nitric acid is well documented [7.35], and the molecular yield (G value) is known to be around 2.0 molecules per 100 eV of adsorbed radiation energy. For inert gas / trace of air systems, the actual yield

will depend on a number of factors, and the products (oxides of nitrogen etc) are in a dynamic equilibrium, with a large set of reactions. However, if there is an end-reaction such as corrosion, consuming nitric acid, then eventually the available (stoichiometric) inventory of nitrogen, oxygen and hydrogen will essentially end up as nitric acid and its corrosion products (nitrates).

Alternatively, if there are other readily corrodible components present (such as deliberately-included oxygen "getters") there will be competing processes acting as a sink for oxygen, particularly. It is a credible scenario that the gas environment becomes a hydrogen – nitrogen mixture, which will radiolyse to give ammonia, rather than oxides of nitrogen [7.36].

The production of nitric acid has been of great concern for the proposed storage of AGR fuel. However, corrosion is dependent upon there being an aqueous electrolyte at the fuel surface – in whatever form that might be (i.e. bulk liquid, condensed droplets, thick adsorbed water layer), as this has some feedback on the required dryness of the fuel store

5.4.3. Corrosion of fuel assembly components in the gas phase environment

5.4.3.1. Fuel surface dryness

In considering dry storage, there is evidently a need to define the dryness of the storage system. In a number of fuel dry storage systems, the fuel is deliberately dried prior to storage (for example at Paks [7.37]). It is normally assumed that water entering the storage environment comes as water associated with the fuel itself, either as

- surface water, in the form of droplets or a liquid film,
- adsorbed water (i.e. attached to the surface by physical forces), or
- absorbed water (i.e. combined into the surface, or surface deposits, by chemical bonding).

In some fuel dry storage systems, the amount of water entering the storage environment can be significant, associated with corrosion product in heavily corroded fuel. (For example, see the Hanford K-basin fuel remediation programme [7.25].) However, in the case of PWR fuel from new-build capacity in the UK, it is assumed that fuel will be intact, and that fuel condition will be of a good quality. This source of water can therefore be ignored.

Furthermore, it is also assumed that for PWR fuel from new-build capacity in the UK, dry storage will be carried out after a period of cooling in the station fuel ponds, an interval of around 15 years after discharge from reactor. At that point the fuel will still be sufficiently radioactive, and possess sufficient decay heat, that on removal from a pond into a gas environment it will self-heat to a temperature of well over 100°C and thereby drive off surface water. (That may not be true for long cooled fuel that has been pond stored for several decades before being transferred to dry storage, so this point should not be completely dismissed.)

Of possible concern is the incidence of water carry over in localised corrosion cells such as bulge joints as discussed in Section 5.3.2.4. Even if the fuel heats to a temperature well above 100°C, any corrosion products which have accumulated within a local cell can be hygroscopic, and retain some measure of moisture at temperatures above 100°C so this effect should also be recognised.

Adsorbed water will be in an equilibrium relationship with the surface, in line with the adsorption isotherm for the relevant humidity and temperature. At a temperature well above 100°C, adsorbed water will be largely evaporated off and will exist in the gas phase. Therefore under that condition surface adsorbed water is not considered viable as an electrolyte to support corrosion. If fuel is long-cooled and at a temperature below 100°C, and depending on the dryness of the gas phase, there may be an equilibrium component remaining on the surface, quite possibly at the molecular monolayer scale. Corrosion due to such water (or nitric acid absorbed within it) is uncertain (i.e. it is uncertain whether it will even be able to function as an electrolyte). As an illustration of this, mild steel irradiated in a flowing air / water vapour mixture experiences a threshold in corrosion rate at about [REDACTED] vpm water vapour (equivalent to about [REDACTED] % RH) [7.38]. The very small amount of corrosion at yet lower humidity is thought to be due to direct reaction with oxides of nitrogen.

Absorbed water includes for example, water of crystallization trapped within the oxide on the metal surface, and within oxides deposited on the surface as crud. These sources of water may well persist at temperatures significantly higher than 100°C. They are firmly bound, in chemical terms, yet may be released by radiolysis of the trapped water producing hydrogen and oxygen, respectively. (Although in practice some of the oxygen is always absorbed by other surfaces, and 2:1 stoichiometry is seldom observed in the gases produced). Nevertheless, these sources of water are unlikely to serve as a functioning electrolyte at $T > 100^{\circ}\text{C}$.

Also of relevance is the design and operation of a dry storage system, in terms of the gas volume in contact with fuel, accessible fuel container surfaces in terms of their materials and surface areas, self-drying time for the fuel and any inert gas flush (and the dryness and pressure of such a gas). There will be several aspects of the dry storage system which are not known at this point in time.

Given these several unknown factors, the actual available water content within a dry storage environment is going to be variable. There is also a possibility that the distribution of water molecules within the system could vary with time, for example water adsorbed on fuel surfaces and container internal surfaces could re-distribute with time as the fuel cools.

As a generalisation, and assuming the fuel to be at a temperature of greater than 100°C through the storage period, it is unlikely that corrosion (in the conventional sense) will be supported by a surface electrolyte layer of water and therefore the only corrosion process will be direct gas phase oxidation of metals. Since the metals involved will already have protective oxide layers, the extent of metal oxidation by general corrosion in this environment is expected to be negligible.

5.4.3.2. Localised corrosion of stainless steel components under dry storage conditions

There is a faint possibility that the stainless steel components might have experienced radiation induced sensitisation, and depending on temperature (and the existence of a surface electrolyte) that could experience corrosion from nitric acid formed by radiolysis of air. Whilst the original temperature (on starting dry storage) may be high enough to avoid corrosion, there is some uncertainty how that changes with time, as temperatures decrease and the water adsorption isotherm changes as a function of temperature.

In the event that such a corrosion mechanism could operate, by virtue of an adequate surface moisture film, then it would be observed as localised corrosion proceeding via intergranular stress corrosion cracking (IGSCC). In turn, that mechanism also requires the presence of a stress force on the sensitised component

5.4.3.3. Zirconium hydriding under dry storage conditions

The potential failure mechanism of delayed hydride cracking has been described in Section 5.2.3. The key feature is the required re-orientation of zirconium hydride platelets as a consequence of thermal cycling. This is a distinct possibility due to the fact that in the first instance, fuel will self-heat on being withdrawn from a pond into the gas phase, due to the reduction in conductive heat removal. Furthermore, drying routines often involve the application of alternating periods of exposure to warm dry gas (such as helium) followed by vacuum. Vacuum will give no conductive heat loss, whereas a gas will give some heat removal: helium is a good conductor of heat, amongst the gases. Therefore temperature cycling is expected, the highest temperatures being in vacuum.

The key temperature for such a re-orientation has been observed as above 275°C [7.39], although in the USA the USNRC have advised that 400°C should be regarded as a limit [7.40]. However, the subsequent hydride cracking process may occur at any temperature down to ambient, and with a delay period built in, hence the phenomenon "delayed hydride cracking" (DHC). Therefore it is clearly important that before any fuel assembly is transferred to a dry storage environment, it must have a residual decay heat production rate below that threshold necessary to reach the appropriate limit when in a dry environment. The exact value of that appropriate limit should be specified in a context relevant to UK dry storage designs and fuel decay heat parameters.

It should also be noted that other stress risers to take into consideration include those occurring under mechanical handling situations, particularly transport accident situations [7.40], for instance if the fuel was being moved from a pond to a dry store. In that study, the particular issue was that fuel pin failure by DHC could result in fuel material experiencing a geometry reconfiguration, with attendant criticality concerns. It is noted in [7.41] that in the USA there are regulatory rules [7.40] which ensure a level of safety under normal dry storage conditions. Similar concern over sudden stress risers having an effect on DHC in zirconium alloy fuel assembly structural components (guide tubes, etc) does not appear to have been recognised.

Recommendation 7.3. Assessment of the effect of thermal cycling on zirconium hydride distribution should be carried out when a drying process is identified and adequate other details are known.

5.4.3.4. Zirconium alloy localised corrosion under dry storage conditions

Section 5.3.2.2 made reference to concentrated salt deposits possibly influencing localised corrosion of zirconium alloys. Whilst that observation [7.31] might also have been explained by hydride cracking, it is noted for reference that concentrated salts could possibly arise in the dry storage process. In dry storage, any surface water on the fuel will be dried off (by self-heating of the fuel, at the least). This will serve to concentrate species during the drying process, but as that will be a relatively short period of time, it is unlikely to produce measurable corrosion. Also the amount of such impurities present in surface water on a fuel element will be low, as the pond water is a controlled environment.

The one instance where this could become a concern is if the fuel is dried (or allowed to self-dry) without first being inverted ("up-ended") to tip out the water within the control rod guide thimbles. In that instance, there could be of the order 400 cm³ pond water within each thimble tube, which would evaporate down to leave an increasingly concentrated solution at the bottom of each thimble, before complete water evaporation. But due to the short timescale for this process, any corrosion consequence is unlikely.

5.5. Discussion of PWR fuel corrosion during extended dry storage

The mechanisms reviewed above make it clear that there are only two credible corrosion mechanisms, namely delayed hydride cracking of zirconium alloys and intergranular stress corrosion cracking of stainless steel.

Of these, the delayed hydride cracking of zirconium alloys is a clear and realistic possibility and needs to be considered carefully. An assessment is made in the following section.

The intergranular stress corrosion cracking of stainless steels is only possible if three conditions are met, namely the irradiation sensitisation of the stainless steel, the presence of a stress field, and an aqueous electrolyte within and around the crack. The irradiation sensitisation of the stainless steel is possible, though unlikely; the presence of a stress field is also possible, due to thermal cycling and expansion / contraction of different metals; the presence of an electrolyte is unlikely, especially for fuel assemblies with a temperature greater than 100°C. The irradiation sensitisation of the fuel, and any built-in stresses are not easily changed after irradiation. But fuel temperature, and store dryness can be predicted and controlled respectively: it is these which influence any surface moisture. Provided these are managed to eliminate an aqueous electrolyte at the stainless steel surface, then intergranular stress corrosion cracking can be mitigated.

5.6. Summary of PWR fuel corrosion during extended dry storage

The very low rates identified for general corrosion of Zircaloy and stainless steel in a gaseous environment mean that general corrosion offers no threat to the integrity of fuel pins or fuel assembly components over the storage time required.

The localised corrosion mechanisms which may apply are:

- delayed hydride cracking of zirconium alloys
- intergranular stress corrosion cracking of stainless steels

6. Assessment of corrosion of AP1000 fuel assembly structural components in long-term storage (Task 8)

6.1. Corrosion susceptibility of spent fuel assemblies

6.1.1. Components considered under this section

The objective of this section is to assess the corrosion performance of spent fuel assemblies, specifically excluding the fuel pins themselves. Therefore it is important, at the outset, to grasp the nature of the fuel assembly without any fuel pins. The skeleton of a fuel assembly consists of the rigid top and bottom nozzles, joined together by the 24 control rod guide tubes and a single instrumentation tube. These tubes are mechanically joined to the top and bottom nozzles by "bulge joints" or screw fastenings, respectively. The guide tubes then carry the pin grids, which are a system of straps and springs to hold and support the fuel pins in place. The afore-going may be considered to be structural components, since if they failed the fuel assembly could lose its integrity. There are other components, attached to the top and bottom nozzles, such as hold-down springs or a grid plate, which are not structural, in the sense that they are not supporting another component. If these were to fail, they may become detached but the fuel assembly would remain essentially intact.

Therefore, priority must be given to assessment of the structural components. By reference to Table 5, the structural components and their materials are as follows:

Control rod guide tubes (or "thimbles")	ZIRLO™ or Zircaloy-4
Bottom nozzle	AISI 304 stainless steel
Top nozzle	AISI 304 stainless steel
Grids (straps and springs)	ZIRLO™ or Zircaloy-4

Other components made of other materials will be considered in passing, but the above represent the key items which will be considered in this assessment.

The corrosion of these materials will now be considered in context, for wet and dry storage regimes respectively.

6.2. Long-term pond storage

6.2.1. General considerations based on past experience

Some of the mechanisms identified above in Section 5.3 may not be operating, or can be ignored, at pond storage temperatures. Westinghouse fuel assemblies have a different top nozzle design to those that failed by IGSCC (see Section 5.3.2.3) so separation of the top nozzle by intergranular stress corrosion cracking need not be considered. Higher decay heat of high-duty assemblies is not considered to be significant given the good heat transfer during wet storage. Because of the low temperatures associated with pond

fuel pins have excellent performance in fuel storage ponds for periods approaching 40 years. As general corrosion rates are so low no problems are anticipated when extrapolating to periods of 100 years storage. Equally no operational problems have been encountered with galvanic and crevice corrosion due to the benign pond water chemistries adopted. Top nozzle separation due to intergranular stress corrosion cracking can also be dismissed as the Unterweser top nozzle design, and material condition, is different to those that failed. Some superficial intergranular attack cannot be discounted as the top nozzle would be expected to have suffered some degree of radiation induced sensitisation. However the integrity of the top nozzle is not considered to be a risk during extended pond storage.

The corrosion protection conferred to AGR fuel by dosing the pond with caustic or nitrate will be equally effective at corrosion protection of the stainless steel and Inconel components of PWR fuel assemblies; any risk of crevice corrosion or intergranular attack should therefore be removed.

6.2.5. General assessment of pond storage corrosion for new fuels

Zircaloy represents a class of materials that are highly resistant to degradation during wet storage. Operational experience and experimental data supports the judgement that satisfactory wet storage of up to 100 years can be achieved in demineralised water. The corrosion data available for zirconium in caustic solutions is limited. Most data relate to much higher caustic concentrations and temperatures than would be experienced during long-term pond storage. On the reasonable assumption that corrosion rates will tend to decrease the lower the caustic concentration and temperature then the lowest corrosion rate can be used although this is still believed to be pessimistic.

The very low corrosion rates identified for Zircaloy and stainless steel mean that general corrosion under normal pond chemistry offers no threat to the integrity of fuel pins or fuel assembly components over the storage time required. Data on zirconium corrosion in caustic solutions are limited. The inferred maximum corrosion rate for caustic pond water of [REDACTED] microns per year (see Section 5.3.2.1) implies [REDACTED] microns metal loss for 100 years storage.

Note that the clad thickness for AP1000 fuel is [REDACTED] microns, and the control rod guide thimbles have a wall thickness of [REDACTED] microns (upper part) and [REDACTED] microns (lower part). The instrumentation tube has a wall thickness of [REDACTED] microns. Therefore a possible metal loss of [REDACTED] microns represents a minimal loss of wall thickness.

No data on zirconium corrosion in nitrate solutions could be found but it is likely that the corrosion rate is the same as in demineralised water. It should be possible to confirm that low Zircaloy corrosion rates exist in caustic and nitrate solutions over short timescales (~ 1 month) using high resolution corrosion probes.

The only forms of localised corrosion that have been observed during the pond storage of LWR fuel are intergranular attack or intergranular stress corrosion cracking (which are discussed in more detail, below). No evidence for irradiation assisted stress corrosion cracking in LWR fuel has been found at Sellafield (but no top nozzles have been subjected to metallurgical examination). As the degree of sensitisation in AGR fuel is greater, any storage regime that preserves AGR fuel pin integrity will also prevent intergranular attack occurring in PWR assemblies. Presuming some measure of co-located pond storage, the introduction of caustic or nitrate inhibitors to prevent corrosion of AGR fuel would be equally effective in preventing corrosion of the stainless steel components of PWR assemblies.

6.2.6. Detailed assessment of pond storage corrosion for new fuels

There are two specific corrosion mechanisms that require assessment, which are

- Delayed hydride cracking of the zirconium-based alloys used in the control rod guide thimbles and the grid straps and springs.
- Intergranular stress corrosion cracking of any stainless steel component (e.g. top nozzle) which has been irradiated within a temperature range of 350 to 520°C.

These are now discussed in turn.

6.2.6.1. Delayed hydride cracking

The mechanism for this form of corrosion has been described above, in Section 5.2.3.

The most important consideration is that the temperature of the fuel must not be allowed to rise to a condition where hydride platelets can re-orientate. The key temperature for such a re-orientation has been observed as above 275°C [8.2], although in the USA the USNRC have advised that 400°C should be regarded as a limit [7.40]. Whilst the fuel is in-pond that is not a possibility, but care should be taken if fuel needs to be transferred between facilities, then water-filled casks should be used to avoid any temporary temperature excursion.

There have been numerous publications evaluating the likely effects of delayed hydride cracking on various fuel systems, including detailed mathematical models. Such modelling lies outside the scope of the present work.

6.2.6.2. Intergranular stress corrosion cracking

The mechanism for this form of corrosion has been described above, in Section 5.2.6.

There is a faint possibility that the stainless steel top nozzle of a fuel assembly may have been irradiated under conditions leading to RIS. There may be some stress associated with the joints between the top nozzle and the zirconium alloy guide tubes. The storage environment in a pond should not be sufficiently aggressive to cause corrosion to initiate and propagate.

This requirement could be met for example by a high chloride content, or an acidic environment. (A standard test for RIS, the "Strauss test" is that the metal is exposed to hot nitric acid; material which has undergone RIS will then corrode rapidly and tests on such coupons are a way of confirming the presence of RIS in a system).

In the context of a well-managed pond with low concentrations of aggressive ions, and an alkaline pH or the presence of other inhibitors, then the initiation and propagation of intergranular stress corrosion cracking should be avoided, even if the material has undergone RIS. Therefore, regardless of fuel history, this mechanism should not apply in a well managed pond.

6.2.7. Conclusions from the assessment of spent fuel in pond storage

Zirconium alloy components such as the control rod guide thimbles may be susceptible to delayed hydride cracking but, provided the fuel temperature is maintained within normal

pond operational limits, in practice this will not pose a threat to the integrity of a fuel assembly.

A specific caution is noted if the fuel is moved between facilities, that water-filled containers or flasks should be used in order to prevent a rise in fuel temperature.

Stainless steel components such as the top and bottom nozzles may be (borderline) susceptible to intergranular stress corrosion cracking. However, regardless of fuel history, the chemistry within a well managed pond should ensure the absence of aggressive species such as nitric acid or chloride ions and so avoid IGSCC or other forms of localised corrosion such as pitting.

6.3. Long-term dry storage

6.3.1. General considerations based on past experience

The dry storage of LWR fuel has been carried out internationally for many years. At every LWR power station there is a cooling pond for the decay cooling of spent fuel, but at many plants the storage of long-cooled fuel has been supplemented by dry storage techniques. These have taken various forms, including vaults, silos, drywells, and casks. The advantages and disadvantages of these various options will not be reviewed here, but it must be noted that the pre-requisite for all of them is that the fuel has been cooled for many years and its radioactivity has decayed to a point where it cannot experience a large temperature rise when transferred from wet to dry storage.

There is however a weakness, in that there has been very little retrieval of dry stored LWR fuel for examination after a significant storage period. The working assumption appears to be that provided various conditions are met (e.g. long-cooled, as mentioned above, and limits on residual water content) there should be no problem and therefore no need to expend the effort and costs associated with an examination of stored fuel. That is consistent with the USNRC view [8.3] that dry storage conditions need only satisfy the requirement that "the spent fuel cladding must be protected during storage against degradation that leads to gross ruptures, or the fuel must be otherwise confined such that degradation of the fuel during storage will not pose operational safety problems with respect to its removal from storage". There appears to be no regulatory requirement for programmed surveillance checking of the condition of dry stored fuel. Two instances of testing of spent nuclear fuel after a period of dry storage have been noted [8.4], [8.5]. The first of these [8.4] was a relatively short (~3 month) test of VVER fuel aimed at examining the fuel for signs of creep, at high temperature, as a verification for the Russian dry storage arrangements. In the event, no signs of creep were found, and some un-identified oval white spots were noted on the cladding, standing out from the dark grey colour which is typical of normal VVER spent fuel. The second test [8.5] was carried out by CRIEPI to review dry stored BWR and PWR fuel, and to compare the BWR fuel with pond stored fuel. The fuel storage period was 20 years. However the BWR fuel in dry storage had been cut into smaller lengths before storage in air, which could have influenced the observations as the fuel matrix itself was exposed to the gas environment and may have reacted preferentially with any acidic species – it was observed to have developed a number of radial crack features. The PWR fuel was one single pin stored in air. It showed no particular feature attributable to dry storage. A puncture test indicated that there had been no significant additional helium release during storage. Zirconium hydride orientation was investigated, with the finding that some orientation redistribution had taken place, with between 15% and 29% of platelets now having orientations within 45° of radial (this from four measurement samples). This result was deemed acceptable

as the relevant Japanese standard sets a limit at 45%. (It compares with a range of 12 to 16% of radial faults at fabrication). The report also calculated a hydrogen redistribution profile (assuming diffusion to cooler parts of the assembly) after 40 years, with the conclusion that it was indistinguishable from the profile after 20 years. (As a point of note, the pond-stored BWR MOX fuel (stored intact for 20 years) showed no visible sign of deterioration: fission product gas release results showed minimal change compared with data from sibling fuel rods measured 20 years previously).

Because dry-stored fuel is by definition less accessible than in a pond, it is clearly far less convenient to carry out even a visual examination. Possibly the easiest fuel to recover and examine, should that be desired, is cask-stored fuel in systems such as the CASTOR flasks used at many European stations, particularly in Germany.

Apart from the requirement for long cooling, mentioned above, the other normal requirement is for residual water content to meet some acceptance criterion. The most widely used criterion is probably the ASTM standard for fuel drying [8.2]. There are possibly some aspects of this standard that need to be applied with care, particularly in the case of drying failed (waterlogged) fuel. This is because the acceptance criterion is based on a pressure recovery measurement, following drying and pumping a vacuum. It is expected that if the water has been effectively removed, then the recovery of a partial pressure based on water vapour will be slow and below a specified rate. However, in the case of waterlogged fuel, there is always the problem of ice formation under vacuum and blocking of any cladding pinhole (or blocking by further corrosion product, or debris), which could give a deceptively low value for a pressure recovery rate whilst water remains within the fuel cladding. It is not the purpose of this assessment to review the ASTM standard, and it would be expected that such obvious problems would be addressed in any process that cites the standard (notwithstanding that the standard comes with various caveats regarding its applicability); this comment is merely that due attention should be given to ratifying whatever water content criterion is adopted for any UK dry storage facility for PWR fuel. In passing, it should also be noted that there also exists an ASTM standard for materials to be used in extended dry storage systems [8.6].

6.3.2. General assessment of the corrosion of key materials in the gas environment

Self evidently, stainless steels and zirconium alloys are highly corrosion resistant and under normal circumstances their corrosion in an air environment will be negligible, even over a 100 year time period. Their corrosion mechanisms are discussed above in Section 5.2.5.

Furthermore, many spent fuel dry stores utilise an inert gas as the medium in contact with the spent fuel, thus further limiting the availability of oxygen to participate in any corrosion process.

The matter becomes more complicated though, with the potential formation of acidic species such as nitric acid, through the action of radiation on nitrogen, oxygen and water, all in the gas phase. Nitric acid may initiate IGSCC on stainless steels but this also requires an electrolytic water layer on the surface and an applied stress. In addition, the transition from a pond store to a dry store can be accompanied by an increase in the temperature of the fuel since the heat sink represented by the pond water is lost. The kinetics of corrosion processes will increase in line with this, a rule of thumb is a doubling of the rate for each 10°C rise. However, temperatures may not exceed 100°C otherwise the surface water (if there ever was any) will have become water vapour, removing the necessary aqueous electrolyte.

Under normal circumstances, zirconium alloys corrode with the formation of a compact and protective oxide layer, ZrO₂. This will be relatively impervious to nitric acid, and

whilst an elevated temperature may result in a thicker oxide film, its protective nature will remain and that will inhibit further corrosion and mitigate failure of the components.

However, a significant increase in temperature will also result in a re-orientation of the existing zirconium hydride platelets. These were naturally formed with an alignment along the existing, co-axial stress fields and in that configuration present no threat to material integrity. However, if re-oriented, then these could align on radial planes, effectively providing crack pathways through the zirconium tube. In this section, we consider only structural components such as the control rod guide thimbles, but the same will also apply to pin cladding. There has been a considerable amount of research on delayed hydride cracking of zirconium alloys in the context of fuel pins, see for example [7.34], [7.39], [8.7] and [8.8]. This possibility will be considered in detail in the following section.

The corrosion of stainless steel in an atmosphere containing nitric acid vapour is not normally of concern, unless the stainless steel has first been sensitised, through Radiation Induced Sensitisation (RIS) and provided there is an aqueous electrolyte in contact with the surface. The incidence of the three contributory factors is as follows.

- The presence of nitric acid vapour in a spent fuel dry store is almost unavoidable, since traces of air and water vapour are always likely to be present, even at very low levels if an inert backfill gas is used.
- It is considered a borderline possibility that some fuel from a high duty core may have been irradiated at temperatures as high as 350°C and thus may have been sensitized.
- The presence of an aqueous electrolyte in contact with a fuel surface can be discounted in fuel which possesses sufficient decay heat to have a surface temperature in excess of 100°C. If fuel were colder than 100°C and if drying had been ineffective, then an aqueous electrolyte at the surface might occur.

The combination of all three requirements being met is unlikely for new build PWR fuel.

The corrosion and failure of sensitised stainless steel items such as AGR fuel pin cladding, is documented in references such as [8.9]. There has been a recent resurgence of interest in potentially dry-storing spent AGR fuel, and a considerable body of relevant work undertaken in the 1990s has recently been reviewed for the NDA, and thereby brought into the public domain [7.38, 8.10, 8.11, 8.12].

Recommendation 8.1. When details of a proposed dry storage container system are known, adequate assessment should be made of the projected gas phase chemistry (including gas reactions in corrosion processes) to reliably predict the environment and any influence on fuel corrosion.

6.3.3. Detailed assessment

Normal atmospheric corrosion of Zirconium alloys and Stainless Steel has very low corrosion rates. Therefore general corrosion of the key fuel assembly components made from these materials will be insignificant and will present no problem. However, there are two localised corrosion mechanisms which can potentially bring concerns over the integrity of key fuel assembly components in dry storage. These are now discussed.

6.3.3.1. Delayed hydride cracking

The basis of this mechanism has been described above. The main issue is that on removal from a pond store to a dry store, spent PWR fuel will experience a rapid increase in temperature, which may cause a re-orientation of the existing zirconium hydride platelets, some of which could end up with orientations radial to the tube section within which they occur (e.g. control rod guide thimble, or fuel pin cladding). The presence of residual stress fields within the structure (e.g. mechanical load, or step-changes in wall thickness) can then cause additional hydriding to occur in that same plane, and as an extension of the existing platelets, such that a crack propagates and results in through-penetration of the zirconium structure.

6.3.3.2. Irradiation-induced intergranular stress corrosion cracking

The basis of this mechanism has also been discussed above, and is expanded in detail in [8.9], [8.10] and [8.12]. The worst possible case outcome from this corrosion mechanism is that the stainless steel top nozzle experiences cracking around the joints to the control rod guide thimbles (tubes) such that the top nozzle will then part company with the remainder of the fuel assembly if subsequently lifted using an attachment to the top nozzle. This could possibly occur in mid-air, as the remainder of the fuel assembly provides a load which would tend to fail any remaining contact, as the assembly became suspended from a hoist.

It has been commented that it is only a borderline possibility that the irradiation temperature could get into a region where RIS might apply. It is certainly true that manufacture techniques have been developed to avoid any thermal sensitisation such as that experienced in the fuel at Prairie Island etc [7.2, 7.32]. Therefore the probability of RIS and any consequent IGSCC must be very low. To fully explore this, some accurate figure is needed for the maximum credible temperature for the top nozzle (it being assumed that the bottom nozzle will be at a rather lower temperature and therefore definitely not a candidate for RIS). To state the known facts: in PWRs the water temperature is approximately 280°C at core inlet and 330°C at core outlet. The maximum fuel cladding temperature is known to be of the order of 360°C or possibly slightly higher. It is then clear that the temperature of the top nozzle will be in the range 330 to 360°C. It is mechanically coupled to the fuel pin, which will facilitate thermal conduction, but of itself the top nozzle is not heat-generating. The actual temperature of the top nozzle could potentially reach 350°C, particularly if the core is pushed in to a high-duty regime. This should be checked against the existing vendor data, and if not available then some thermal-hydraulic assessment should be undertaken. Provided that it can be demonstrated that the required temperature for RIS has not been achieved, then this corrosion mechanism can be dismissed.

6.3.4. Conclusions from the assessment of spent fuel in dry storage

There are two localised corrosion mechanisms which may apply to spent PWR fuel in dry storage, namely:

- Delayed Hydride Cracking (DHC) of zirconium-alloy components such as control rod guide thimbles, or fuel pin grids
- Intergranular Stress Corrosion Cracking (IGSCC) of stainless steel components, particularly the top nozzle

It has been concluded that provided the fuel is sufficiently long cooled before transfer from pond store to dry store, such that the inevitable temperature increase results in a value less than the threshold required for re-orientation of pre-existing zirconium hydride platelets, then no detriment to the fuel should result and no DHC should be observed.

It has also been concluded that provided it can be clearly demonstrated that the top nozzle does not experience temperatures of 350°C or greater, even under high-duty core conditions, then the incidence of radiation induced sensitisation (RIS) can be discounted and consequently the risk of IGSCC is also mitigated.

7. Estimation of conditions prevailing in fuel crud (Task 9)

In order to assess the influence of crud on any subsequent corrosion behaviour in storage, a short description of PWR crud is now made. The morphology of PWR fuel crud has recently been explored in far more detail than in the previous decades of PWR operations. A number of factors have contributed to this recent increase in interest, associated with the potentially increased deposits as cores are pushed to higher duty (with possibly associated higher incidence of boiling), and the appearance of the axial offset anomaly (AOA) effect which is linked to a boron component within the fuel crud. Yet further interests stem from the potential to influence fuel crud by the addition of coolant additives such as zinc or noble metals.

Further possible corrosion mechanisms include those which take place within occluded cells beneath the cover of a deposited crud layer. There have been indications that crud layers on Zircaloy clad fuel tend to soak loose during long periods of wet storage [7.9]. This suggests that future fuel handling operations may need to include assessments of the impact of loosened crud layers. This observation raises the whole question of the nature of the crud layer on the surface of Zircaloy clad fuel. The observations from current plant have been reviewed and summarised by Byers and Deshon [9.1] — the general features of the surface oxide and crud layer are as follows.

- The zirconium alloy fuel cladding carries a surface layer of zirconium oxide.
- On top of the zirconium oxide is a crud layer which consists mainly of nickel oxide and iron oxide. (This is true of plants having nickel-based alloys in the steam generator tubing). The crud layer thickness can vary between ten and a hundred microns.
- Some zirconium oxide is also found in the crud layer. Various composite mineral phases are identified, including bonaccordite.
- In some cases, boric acid or lithium tetraborate may be present in certain spans of the fuel, correlated with specific temperature and flow regimes, particularly for high-duty plant when under irradiation. These deposits dissolve at lower temperatures and are not present in stored fuel.
- The morphology of the crud can be porous: when in the reactor and subject to a heat flux, localised boiling occurs within the pores which act as wick-boiling chimneys.

Reference [9.1] also provided an image of a cross-section through PWR crud from the Callaway reactor, shown in Figure 11. Note that this is an extreme example in terms of crud thickness. More normally, crud layers would be of the order 10 to 15 microns thick, for non-AOA plant.

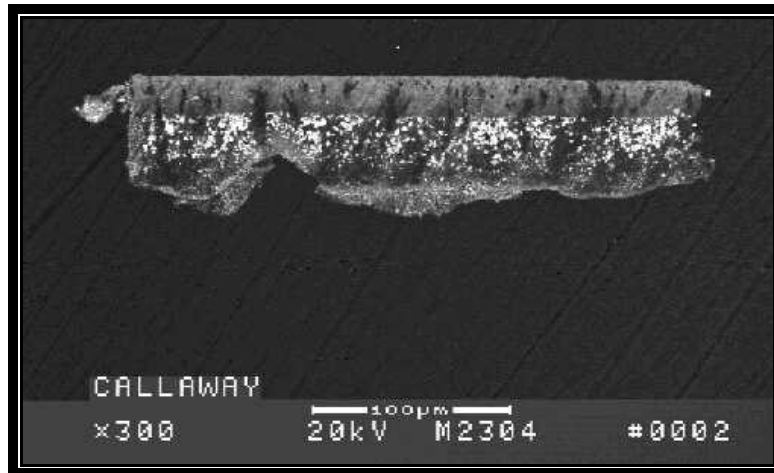


Figure 11: SEM of crud from the Callaway Cycle 9 core (cladding interface at top of deposit)

In [9.1] they note that in this backscattered electron image, the brightest particles at the centre of the deposit were composed of zirconium oxide. It was interesting that the layer closest to the cladding had a very low zirconium oxide content, and this layer was also enriched in iron. The outermost layer (away from the cladding interface) was rich in nickel. Also visible are the pores within the deposit, indicative of the “steam chimneys” that form during operation which facilitate boiling of the water which permeates the deposit.

The consequences of crud build-up are recognised to be important and are addressed in WCAP-12610 [6.7].

One further possible complication with fuel crud is the addition of zinc to the reactor coolant. This practice is becoming widespread, but has not explicitly been proposed for the UK AP1000. In the event that zinc is added, then it becomes incorporated in surface crud and corrosion product layers, in a mineral phase known as Trevorite. The consequences of zinc addition on fuel long-term storage would need to be considered if that option were to be pursued. However, it should be noted that ZIRLO™ clad fuel has been successfully irradiated in the Diablo Canyon 2 PWR under coolant conditions including zinc addition [9.2].

8. ENIGMA calculations of corrosion film thickness (Task 10)

Task 6 involved assessing cladding integrity during long-term wet and dry storage. As noted in Section 4.1, this assessment assumed no crud formation, since this is consistent with Westinghouse claims for no crudding in the AP1000, and a cycle-averaged lithium concentration of [redacted] ppm.

Since the absence of crud cannot be confirmed at this stage, with no AP1000s operating in either the UK or elsewhere, and since the UK AP1000 water chemistry regime is not yet finalised, a short investigation of the effects of crud and coolant lithium concentration on (end of irradiation) clad oxide thickness is performed in this section.

Two additional ENIGMA runs were performed which utilised the nominal run used to determine the cladding state after irradiation (described in Section 4.1) as a starting point. In the first run the coolant cycle-averaged lithium concentration was doubled from its nominal value to [redacted] ppm. In the second run a 15 micron crud thickness was modelled (conservatively throughout irradiation, i.e. assuming quasi-instantaneous formation). The crud thickness chosen is a typical value obtained from crud scrapes of fuel operating in current US PWRs that do not experience an axial offset anomaly [9.1]. The clad oxide thickness results from the two runs are reproduced in Figure 12.

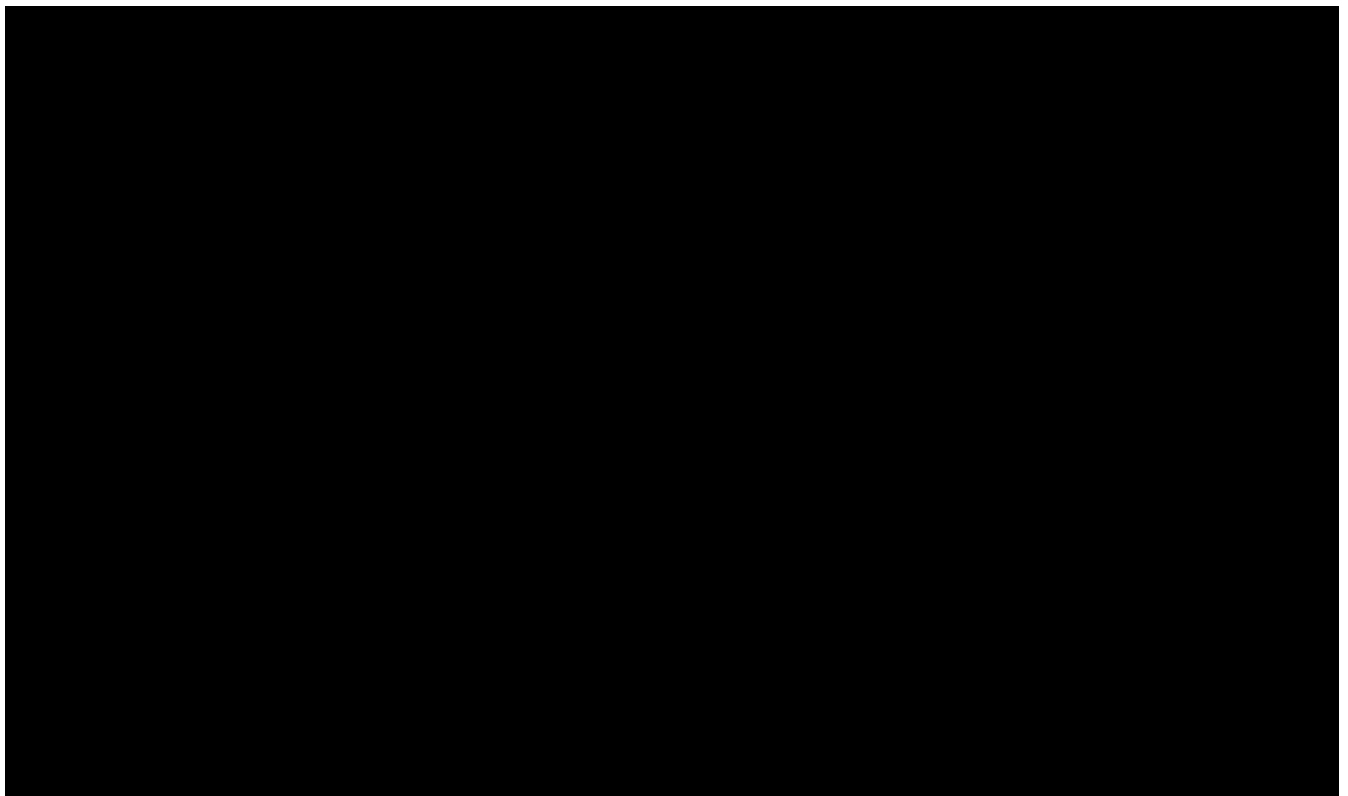
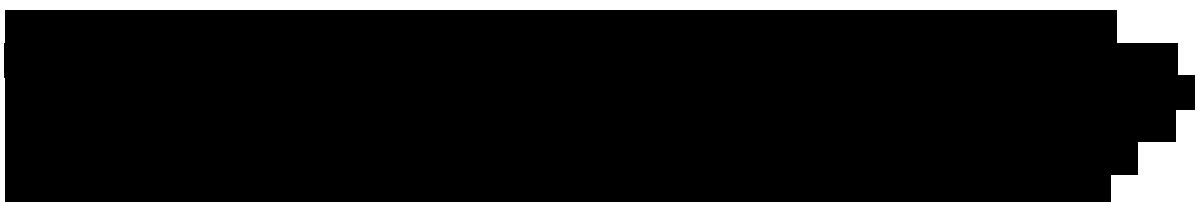


Figure 12: Clad oxide thickness versus distance from bottom of fuel stack with a [redacted] ppm cycle averaged lithium concentration and with 15 microns crud



[REDACTED]

[REDACTED]

[REDACTED]

9. Conclusions

The limited data available suggest that general corrosion rates of zirconium alloys and stainless steel in long-term wet storage are very low and pose no threat to component integrity over the storage times required. Due to in-reactor effects, fuel cladding ductility will be reduced, but no further change is expected to occur at pond storage temperatures. With specific regard to fuel ponds operating at high pH, due to the possible co-location of PWR and AGR fuel, it is noted that corrosion rate data for zirconium alloys in caustic solutions is extremely limited. The inferred maximum corrosion rate in caustic pond water of [REDACTED] microns per year implies [REDACTED] microns metal loss during 100 years storage. The other possible feature of ponds including co-located AGR and PWR fuel is the addition of corrosion inhibitors such as nitrate ions. No corrosion rate data for zirconium alloys in nitrate solutions has been found. However, it is considered reasonable to assume that corrosion rates are unchanged from those in demineralised water.

Degradation mechanisms relevant to long-term dry storage (including the pre-storage assembly drying) include clad creep, localised corrosion of sensitised stainless steel, and hydride attack of irradiated zirconium alloys. Calculations using NNL's ENIGMA fuel performance code have indicated that [REDACTED]

[REDACTED] However, the ENIGMA calculations assumed no crud formation on the cladding surface, and a sensitivity study suggested that [REDACTED]. It is considered that irradiation conditions will be borderline for the possible onset of radiation induced sensitisation (RIS) in stainless steel, which could render the components vulnerable to attack by nitric acid (formed by radiolysis of moist air). However, the probability is that RIS conditions will not be met, and the likelihood of this mechanism occurring is therefore low. With respect to zirconium alloy components, the re-orientation into a radial geometry of zirconium hydride platelets formed during irradiation can lead to embrittlement or delayed hydride cracking, both of which can threaten component integrity. However, the probability of structural component failure by this means is considered low, and ENIGMA calculations indicate that [REDACTED]

[REDACTED]. Firmer conclusions on dry storage can generally only be drawn once dry storage and assembly drying systems are defined.

■ [REDACTED]

[REDACTED]

[REDACTED]

[REDACTED]

[REDACTED]

[REDACTED]

[REDACTED]

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Appendix A: Simulation of assembly drying operation

Prior to dry storage of fuel assemblies, a transfer cask assembly must be loaded with assemblies under water, drained, and then subjected to a drying operation. The transfer cask assembly consists of a spent fuel canister — also known as a basket, multi-element bottle (MEB), or multi-assembly sealed basket (MSB) — mounted inside a transfer cask. The drying operation removes residual moisture from the canister in order to minimise corrosion and canister pressurisation during dry storage. Purge drying — where an inert gas sweeps moisture from the canister — is possible, but vacuum drying — where the canister interior is pumped down to vacuum conditions — is the technique generally used due to the greater effectiveness [A.1]. Vacuum drying is therefore assumed here.

The standard procedure for vacuum drying and subsequent dry storage of LWR fuel assemblies would include a drying operation for intact fuel assemblies (as of interest here) that consists of the following steps (as, for example, the Trojan PWR independent spent fuel storage installation in Oregon [A.2]):

1. loading of transfer cask assembly with a given number of fuel assemblies determined by the cask design (in stagnant water, fuel assemblies taken from spent fuel pond and moved by crane into transfer cask assembly in a cask loading pit);
2. lifting of transfer cask assembly from cask loading pit and draining of volume between spent fuel canister and transfer cask (in air);
3. movement of transfer cask assembly to a decontamination and assembly station (in air);
4. washing of transfer cask and attachment of vacuum drying system (in air);
5. draining of spent fuel canister, welding of canister shield and structural lids, weld testing (including pressure tests in water and/or helium);
6. vacuum drying of spent fuel canister (potentially with multiple cycles of evacuating to the target near vacuum pressure, holding with all ports closed, and flushing with helium);
7. backfill of spent fuel canister with helium;
8. welding of cover plates and ports and weld testing (in air);
9. transport of transfer cask assembly to dry storage system location (in air);
10. transfer of spent fuel canister from transfer cask to dry storage system (in air).

It is important to note that it is the spent fuel canister which is the sealed container during dry storage (and which is sealed in step 8). The dry storage system refers to the system in which the spent fuel canister is dry stored, which could be a dry storage cask, a vault, or a modularised storage system such as the NUHOMS concept [A.8]. It is possible in the above that the transfer cask is also the dry storage cask, in which case step 10 would be omitted.

The steps above are used as the basis for the discussion below, although it is recognised that the actual processes for a new build LWR will likely include some modifications to the above.

Due to the decay heat and the absence of conductive and convective heat transfer from the fuel rods to the surroundings (ignoring any heat transfer due to the evaporation of water), the clad temperatures will rise from their initial values during each evacuation and hold phase of the drying process. At any given elevation, the clad temperature will stabilise when the decay heat generation rate is balanced by the radial heat transfer rate to the surroundings due to radiation. For each assembly, the eventual peak steady-state clad temperature, i.e. the maximum steady-state clad temperature at any elevation,

experienced will depend primarily on the total decay heat load of the cask (although the cask design, the assembly design and the decay heat distribution are also important). The total decay heat load of the cask in turn depends upon the number of assemblies in the cask, and, for each assembly, the pre-drying cooling time, the fuel burnup, and the fuel enrichment. For example, the peak steady-state temperature in a (moderately sized) TN-24P cask containing 24 PWR assemblies is [redacted] °C with a [redacted] kW heat load [A.3], whereas the equivalent temperature in a (large) TN-32 cask containing 32 PWR assemblies is [redacted] °C for a [redacted] kW cask heat load [A.4].

Since it is only during the vacuum drying itself, i.e. step 6, that elevated clad temperatures are experienced, it is only step 6 that is simulated. The details of the simulation (which is for the lead rod) are described below.

The rod external pressure is set to zero, as per vacuum conditions. The ambient temperature, $T_{ambient}$, is set to 100°F, or 37.8°C, which is a typical value used in cask licensing. The imposed peak clad surface temperature versus time profile consists of: (a) a heat-up from the spent fuel pond temperature to the peak steady-state temperature, T_{peak} ; (b) a hold at this temperature; and (c) a quasi-instantaneous decrease to the peak initial dry storage temperature (in helium). The peak clad surface temperature axial zone (henceforward referred to as the peak axial zone) is that with the maximum local decay heat load per unit length, q_{peak} . The clad surface temperature, T_z , in each of the other axial zones is modelled assuming clad surface temperature minus ambient temperature is proportional to local decay heat load per unit length, q_z , i.e.

$$T_z = (T_{peak} - T_{ambient}) \frac{q_z}{q_{peak}} + T_{ambient} \tag{A1}$$

The total time for (a) to (c) is taken to be 24 hours, which should bound the total time for the majority of vacuum drying procedures (the drying operation for fuel from the Trojan PWR has been estimated to take 10 to 16 hours [A.2], while German experience with CASTOR cask loading at the Würgassen BWR gives a cycle length of 2 to 5 hours [A.1], and only one, two or three cycles would be expected). This is also consistent with the drying time assumed in previous BNFL analyses of dry storage [A.5,A.6] and in a study by Rashid and Machiels [A.7].

Since the 24 hour drying time would in reality include multiple evacuation/hold/flushing cycles, there is an implicit conservative assumption in the modelling that any flushings and re-evacuations have an insignificant effect on the cladding temperatures. This conservative assumption also justifies not simulating drying times greater than 24 hours, which are possible, since these longer drying times would by necessity be associated with a significant number of cycles.

[redacted]

[redacted]

[redacted]

For simplicity, the approximation is made that the heat-up times in the remaining axial zones are equal to the heat-up time in the peak axial zone.

The peak clad temperature is calculated on the basis of published data on peak clad temperature minus ambient temperature versus cask heat load per unit length (for which there is expected to be a reasonable correlation on theoretical grounds). The data used [A.2,A.3,A.4,A.8,A.9] are plotted in Figure A1, [REDACTED], and approximate upper and lower limit curves suggested by the data (dashed lines, corresponding to +/- 25% on peak clad temperature minus ambient temperature). Each dataset is labelled according to the cask type[‡], with the number of loaded fuel assemblies and the fuel assembly type in brackets.

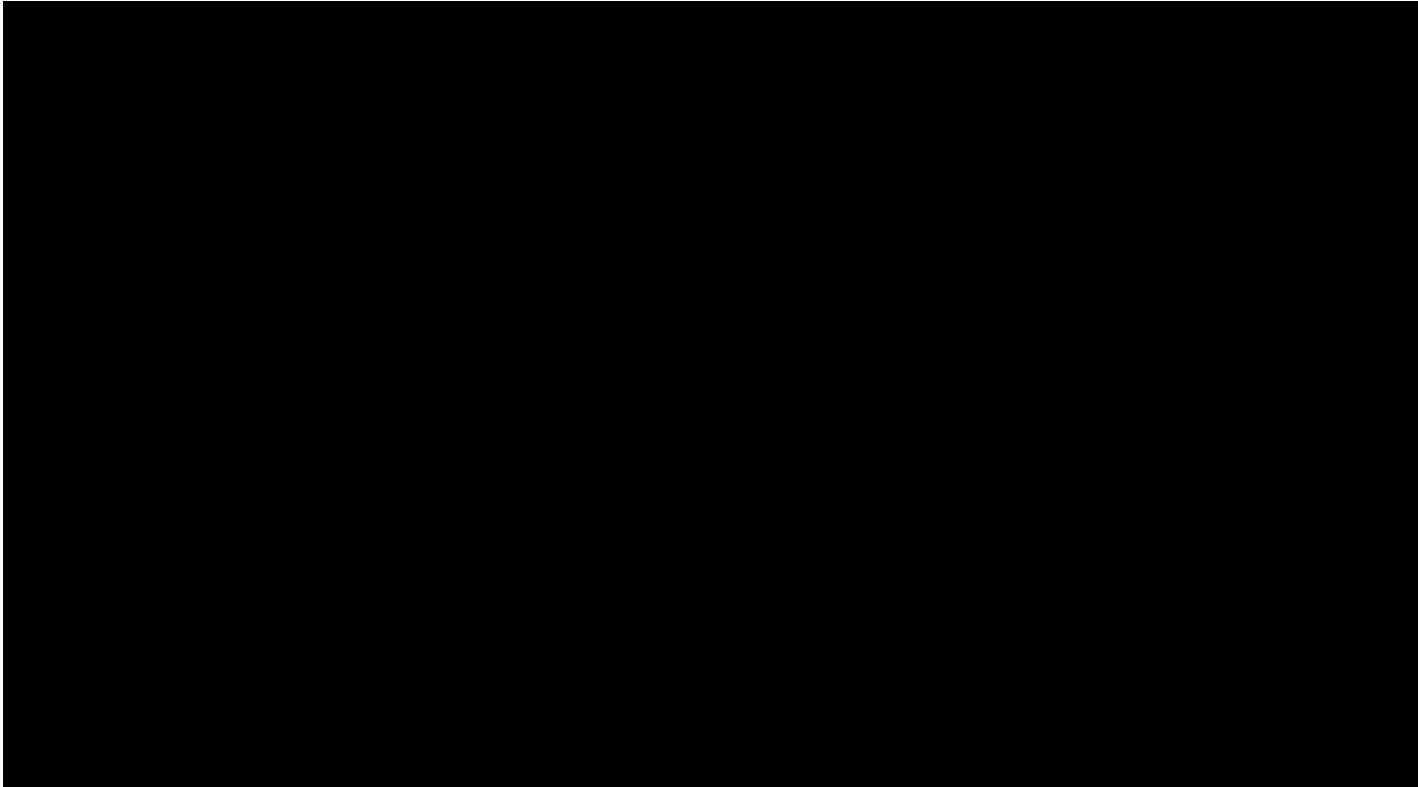


Figure A1: Peak clad temperature minus ambient temperature versus cask heat load per unit length for vacuum drying operations

[REDACTED] The cask heat load per unit length is calculated assuming a cask loaded with 24 assemblies which are all at the maximum burnup considered in this study of 65 GWd/tU (and therefore all have the maximum possible decay heat after the several years of pond storage being considered here). The (decay) heat load per fuel assembly is computed by the FISPIN code, as described in Section 3. Modelling a cask with 24 assemblies is consistent with the highest burnup NUHOMS system (NUHOMS 24PTH, licensed up to 62 GWd/tU) and the high burnup TN 24 system for extra long fuel (TN 24 XLH, licensed up to 55 GWd/tU). Assuming all assemblies are at the maximum 65 GWd/tU burnup is conservative, since, in reality, a cask loading strategy would likely be employed to mix assemblies of different burnups, thereby significantly reducing the maximum cask heat load. The assumption also simplifies the calculations (since FISPIN calculations are only required for one assembly burnup value) and is consistent with the EPR final geological disposal assessment [A.10].

During the drying procedure, the assemblies will be in a vacuum or a helium cover gas (albeit with some residual moisture) and the total drying time is relatively short. Thus,

[‡] Strictly, the NUHOMS HD is not a cask type, but a type of (modularised) dry storage system. However, for simplicity, this distinction is ignored in this appendix.

despite the relatively high clad temperatures, no clad corrosion is expected. The ENIGMA clad corrosion model is therefore deactivated during the simulation of drying.

It should be emphasised that the equation used to calculate peak clad temperature minus ambient temperature as a function of cask heat load per unit length is empirical, and is applied generically irrespective of the actual transfer cask assembly design, which has not yet been defined. Once the design is finalised, a more accurate calculation of clad temperatures is recommended using a computational fluid dynamics code (such as FLUENT) and/or an appropriate subchannel thermal-hydraulics code (such as COBRA-SFS). The impact of the revised temperatures on cladding creep would then need to be assessed. It is important that any code used for these calculations has been suitably validated for spent fuel drying and/or storage scenarios; the validation database should ideally include temperature measurements from experiments performed using a cask of the chosen design.

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Appendix B: Out-of-pile creep equation

Key to the assessment of clad deformation during dry storage is the availability of a suitable creep equation. The model used in ENIGMA is based on the work of Bouffieux, Limon et al [B.1,B.2], which other groups working on similar assessments of dry storage behaviour cite as the state-of-the-art model for out-of-pile creep of Zircaloy-4 cladding, see for example publications by CEA [B.3], EPRI [B.4] and CIEMAT [B.5].



To examine how the model performs in practice consider first Figure B1.

Figure B1 shows this, for one hundred years of straining at constant stress and temperature, with strain limits of one, two or five percent. The region to the left and below the lines on Figure B1 illustrates the acceptable regime of stress and temperature in which rods would not be expected to fail due to excessive creep strain. The one percent strain value is the usual choice of design limit; this is very conservative compared with the real ductility of Zircaloy, even for highly irradiated material, which is typically a few percent. The scales in Figure B1 are chosen to show the full range of stresses and temperatures that are relevant to dry storage. Separate design limits, other than creep strain, are imposed to prevent temperatures exceeding 400°C or stress exceeding 120 MPa.

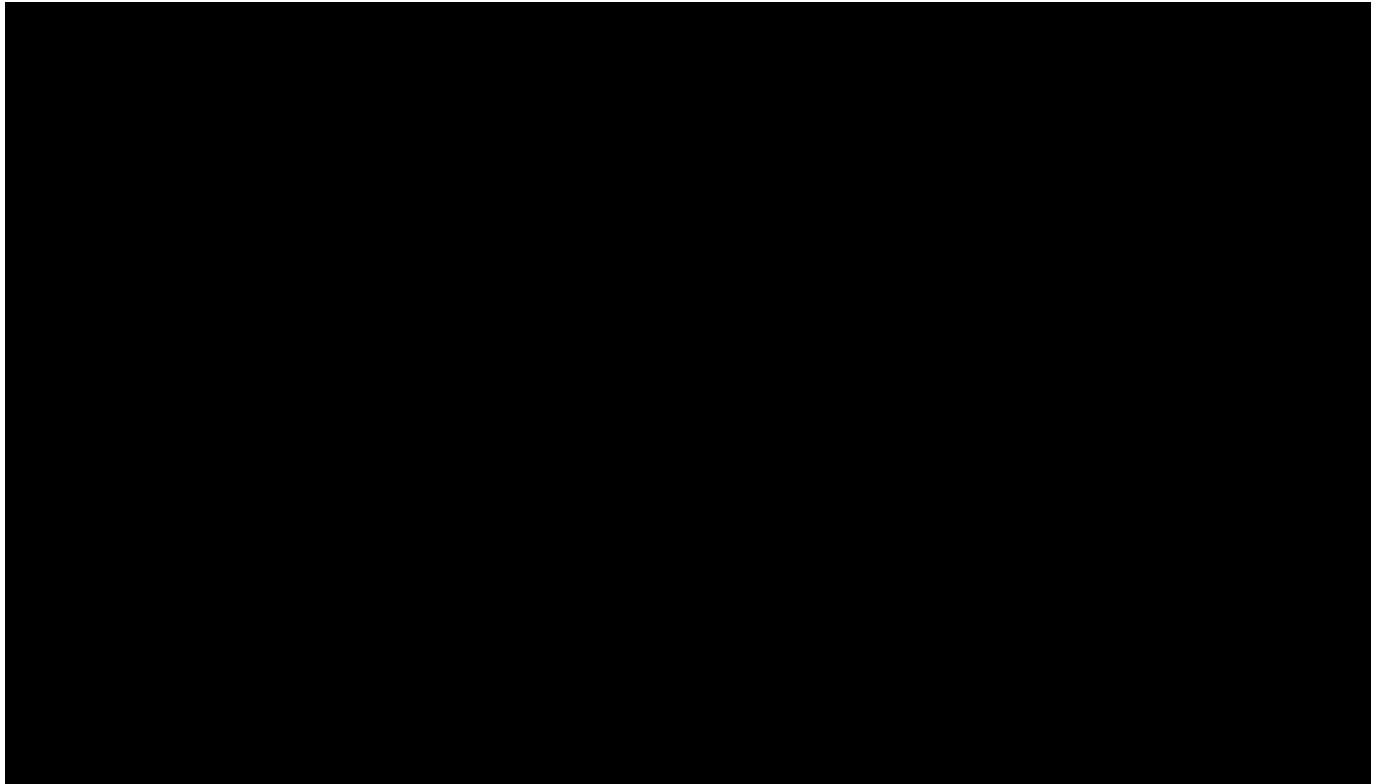


Figure B1: Strains produced after one hundred years at constant stress and temperature, considering secondary creep only

To recap, Figure B1 shows a simplified treatment in which primary creep is ignored. Now consider Figure B2. The dashed green line is the same as on Figure B1, showing the combinations of stress and temperature that lead to one percent strain after one hundred years, assuming only secondary creep. The solid green line (which can only be generated by an iterative numerical solution) shows how this changes when the primary creep term is included; as would be expected for the situation where stress is constant (or reducing), the contribution from primary creep is relatively small.

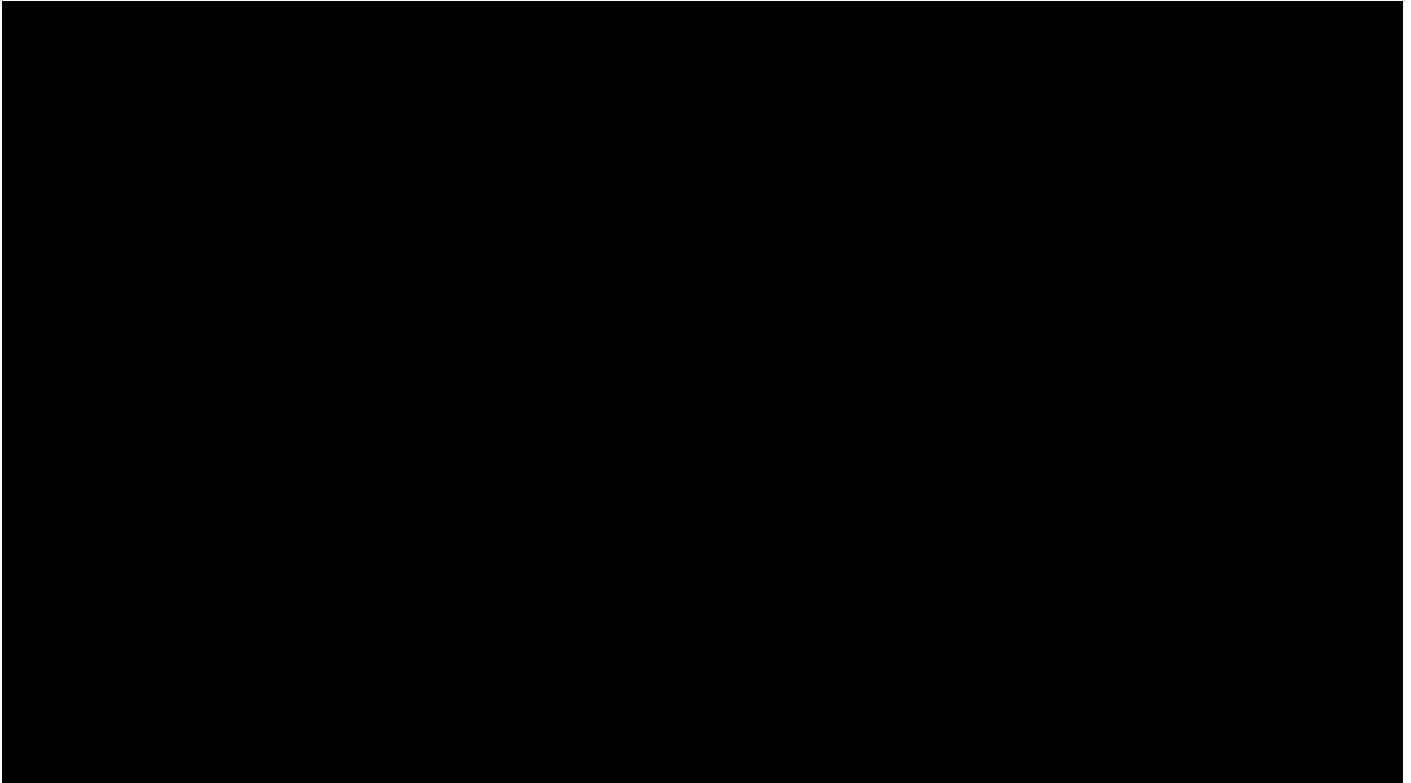


Figure B2: As above, but illustrating: (a) the contribution of primary creep; (b) the difference between the properties of fresh and irradiation-hardened material

The effect of irradiation by fast neutrons is to harden the material, and this effect is quite marked. The red lines in Figure B2 show the same calculation of one percent strain over one hundred years, but for a fast fluence level of 10^{22} n/cm² (as would be experienced by PWR fuel rods at around 60 GWd/tU burnup). Clearly, if the creep properties of irradiated cladding could be assumed when assessing dry storage, then margins to failure would be significantly larger.

However, this is not the usual assumption. Immediately after irradiation, the creep properties of cladding could be expected to match those represented by the irradiation-hardened equation, however any subsequent excursion to high temperature, such as during the vacuum drying of fuel assemblies, could lead to the annealing out of irradiation damage (though some of the hardening is also due to the presence of hydrogen, which will not be annealed). Attempts to model the kinetics of the annealing process have been published, such as by Rashid and Machiels [B.4], but no model has yet been incorporated into ENIGMA. Instead, ENIGMA offers the user the option to choose between using the hardened or the fresh forms of the creep equation, moreover this selection can be made at each individual timestep of the post-irradiation history being modelled. Thus, the early stages after discharge can be modelled using the hardened creep equation, but then after a period at high temperature the creep properties can be re-set to those of fresh cladding. Clearly, a more conservative result is produced by assuming that the clad creeps as per fresh material during dry storage, and hence this is the usual basis of analysis on the grounds of conservatism.

Finally, it should be noted that ENIGMA uses the usual strain-hardening assumption when applying the above creep law under conditions of varying stress and temperature. That is, after a period of straining at one stress and temperature, an effective starting time is determined that would give the same strain value at the new level of stress and

temperature, the strain increment for the new step is then calculated using this effective starting time. The effective time calculation requires the creep equation to be inverted numerically, which ENIGMA accomplishes using Newton-Raphson iteration with a starting guess based on first order expansion of the logarithmic term.

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Appendix C: Simulation of dry storage

Dry storage of spent fuel assemblies is possible in vaults, silos, or casks (including metal and concrete variants). Vaults are sub-surface storage systems, which are also known as dry wells. Silos are modularised at-surface storage systems, which can either be contained within a building (a dry store) or be in the open, e.g. the NUHOMS system [C.1]. Further information on dry storage concepts can be found in an IAEA survey [C.2].

The most likely dry storage system for new build LWRs would be casks or a NUHOMS-type silo. These both have the following features: (a) a sealed spent fuel canister — also known as a basket, multi-element bottle (MEB), or multi-assembly sealed basket (MSB) — with a helium cover gas; (b) a metal or concrete outer shell surrounding the spent fuel canister; (c) cooling by natural circulation of air in the annulus between spent fuel canister and shell, or at the shell outer surface. Thus, a single dry storage simulation can be performed to approximately cover both these system types; this is the simulation (for the lead rod) performed in this study.

The decay heat produced by the fuel assemblies in each cask or silo module is dissipated by a combination of conduction, natural convection and radiation. The extent of cooling due to natural convection would be expected to be dependent upon the orientation, i.e. vertical or horizontal, of the cask or silo module. However, temperature measurements in casks and NUHOMS modules containing irradiated fuel assemblies have shown that the peak clad temperatures are only slightly affected by the orientation, and that there is not a general trend for increased temperatures with a particular orientation [C.3]. Thus, conduction and, to a much lesser extent, radiation, appear to be the dominant modes of heat transfer.

At any given elevation during steady-state conditions, the decay heat generation rate for each rod is balanced by the radial heat transfer rate to the surroundings due to conduction and radiation. For each assembly, the peak steady-state clad temperature, i.e. the maximum steady-state clad temperature at any elevation, experienced will depend primarily on the total decay heat load of the cask or silo module (although the cask or silo module design, the assembly design and the decay heat distribution are also important). The total decay heat load of the cask or silo module in turn depends upon the number of assemblies in the unit, and, for each assembly, the pre-drying cooling time, the fuel burnup, and the fuel enrichment. For example, the peak steady-state temperature in a (moderately sized) TN-24P cask containing 24 PWR assemblies is [redacted] °C with a [redacted] kW cask heat load [C.3], whereas the equivalent temperature in a (large) TN-32 cask containing 32 PWR assemblies is [redacted] °C for a [redacted] kW heat load [C.4].

The pressure boundary condition at the rod surface is set to an atmospheric value. The ambient temperature, T_{ambient} , is set to 100°F, or 37.8°C, which is a typical value used in cask licensing.

The peak clad surface temperature, T_{peak} (during steady-state conditions) is calculated on the basis of published data on peak clad temperature minus ambient temperature versus cask or silo module heat load per unit length. The predominant radial conduction heat transfer from a fuel rod to its surroundings (see above) suggests that there should be a reasonable correlation between these two quantities. The data used [C.1, C.3-C.8] are plotted in Figure C1, [redacted] and approximate upper and lower limit curves suggested by the data (dashed lines, corresponding to +/- 25% on peak clad temperature minus ambient temperature). Each dataset is labelled according to the cask or silo module type, with the number of loaded fuel assemblies and the fuel assembly type in brackets. Only data for LWR assemblies in casks or the NUHOMS silo with a spent fuel canister helium cover gas are included. The data cover casks holding between 19 and 52 assemblies, inclusively. Additional data for cask designs holding one or twelve assemblies were also available. However, these additional data were rejected, since a different trend exists for these small cask types, which are, in any case, un-prototypic of current cask designs.

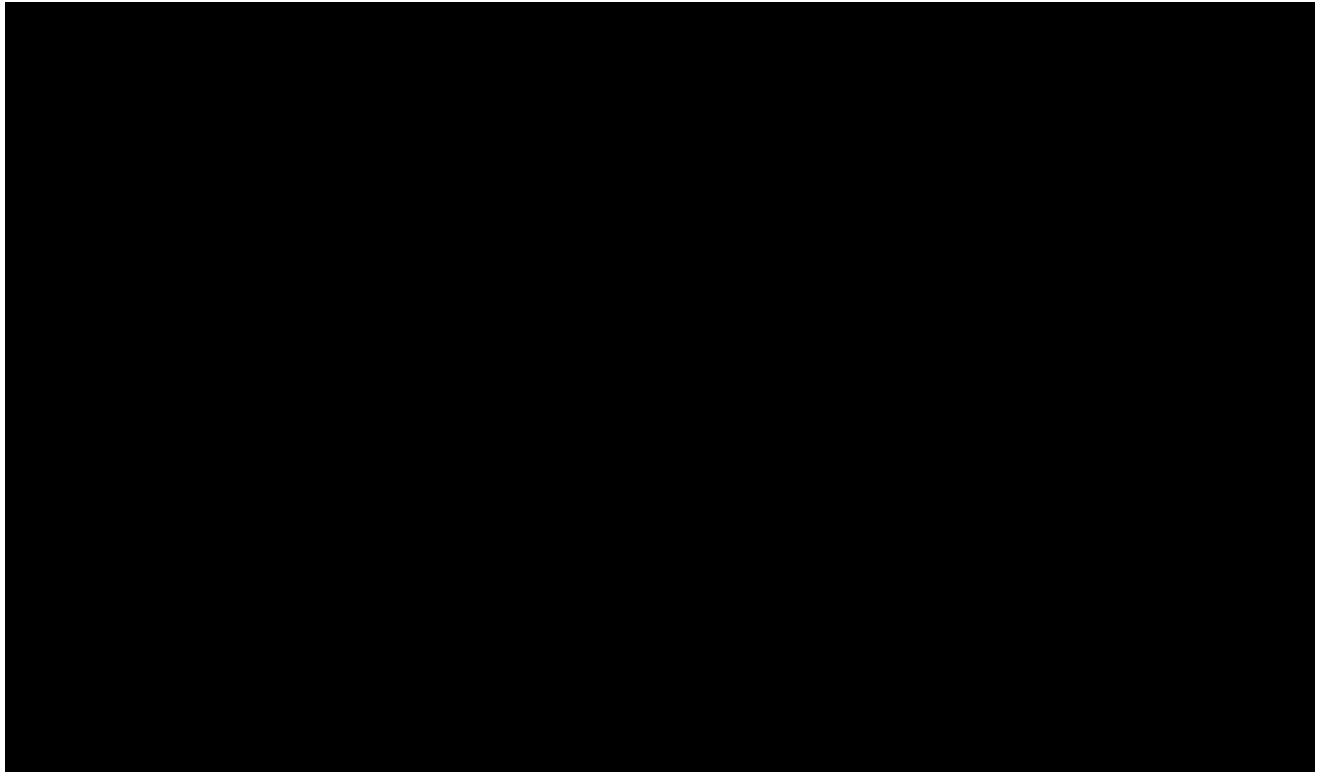


Figure C1: Peak clad temperature minus ambient temperature versus cask or silo module heat load per unit length for dry storage

The cask or silo module heat load per unit length is calculated assuming loading with 24 assemblies which are all at the maximum burnup considered in this study of 65 GWd/tU (and therefore all have the maximum possible decay heat after the several years of pond storage being considered here). The (decay) heat load per fuel assembly at any given time during dry storage is computed by the FISPIN code, as described in Section 3. Modelling a cask or silo module with 24 assemblies is consistent with the highest burnup NUHOMS system (NUHOMS 24PTH, licensed up to 62 GWd/tU) and the high burnup TN 24 system for extra long fuel (TN 24 XLH, licensed up to 55 GWd/tU). Assuming all assemblies are at the maximum 65 GWd/tU burnup is conservative, since, in reality, a cask or silo module loading strategy would likely be employed to mix assemblies of different burnups, thereby significantly reducing the maximum combined heat load. The assumption also simplifies the calculations (since FISPIN calculations are only required for one assembly burnup value) and is consistent with the EPR final geological disposal assessment [C.9].

The peak clad surface temperature axial zone (henceforward referred to as the peak axial zone) is that with the maximum local decay heat load per unit length, q_{peak} . The clad surface temperature, T_z , in each of the other axial zones is modelled assuming clad surface temperature minus ambient temperature is proportional to local decay heat load per unit length, q_z , i.e.

$$T_z = \left(T_{peak} - T_{ambient} \right) \frac{q_z}{q_{peak}} + T_{ambient} \tag{C1}$$

During dry storage, the assemblies will be in a helium cover gas with negligible residual moisture (due to the vacuum drying procedure). The clad temperatures will also decrease with time from their initial dry storage values due to the reduction in decay heat with time. Thus, despite the relatively high initial clad temperatures, no clad corrosion is








expected. The ENIGMA clad corrosion model is therefore deactivated during the dry storage simulation.

It should be emphasised that the equation used to calculate peak clad temperature minus ambient temperature as a function of cask or silo module heat load per unit length is empirical, and is applied generically irrespective of the actual cask or silo module design, which has not yet been defined. Once the design is finalised, a more accurate calculation of clad temperatures is recommended using a computational fluid dynamics code (such as FLUENT) and/or an appropriate subchannel thermal-hydraulics code (such as COBRA-SFS). The impact of the revised temperatures on cladding creep would then need to be assessed. It is important that any code used for these calculations has been suitably validated for spent fuel storage scenarios; the validation database should ideally include temperature measurements from experiments performed using a cask or silo module of the chosen design.

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