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Mail Stop O13-D13
Washington, DC 20555

Subject: W. Hodges' Request for Clarification

Dear Kim:

This letter is intended to provide some supplemental information on material presented to the Staff of the Spent Fuel Project Office on July 10, 2002. The request for some supplemental information was made by W. Hodges to A. Nelson on July 11, 2002.

1. Temperature Limits

High enough temperatures, or sufficiently long times at elevated temperature have the potential for inducing physico-chemical changes in the spent-fuel cladding. Changes that have been discussed are the results of the following processes:

- Annealing of irradiation-induced defects such as point defects and loops
- Annealing of cold work, i.e., lowering in dislocation density
- Recrystallization, i.e., further lowering in dislocation density and changes in grain morphology

These processes introduce changes in the cladding, which are irreversible. For example, point defects (interstitials and vacancies) that have recombined due to their increased mobility resulting from higher temperatures do not regenerate upon cooling. Once they are recombined, they stay that way.

Other changes are driven not only by higher temperatures, but also by the subsequent cooling cycle. The specific process that was addressed at the July meeting was the re-dissolution of hydrides upon heating followed by re-precipitation of the hydrogen upon cooling.

Mechanical properties of the cladding will be modified to some extent by these processes. The changes in mechanical properties have the potential to be beneficial, deleterious, or indifferent depending on the specific scenario challenging cladding integrity. These scenarios include consideration, for examples, of cladding creep under normal and off-normal conditions, or cladding response to impact loads for a spectrum of hypothetical accident conditions.

Independent of the consideration of other important variables (such as hoop stress), any deformation by creep and any re-orientation of hydrides due to the heating-cooling temperature cycling can be minimized by keeping cladding temperature "low" (to be defined). Conversely, sufficiently long times at elevated temperature may have beneficial effects, for example, when the cladding is challenged by axial bending.

Deformation due to Creep

EPRI report 1003135 [Creep Modeling and Analysis Methodology for Spent Fuel in Dry Storage] provides a robust technical basis for an upper temperature limit of 400°C for spent high-burnup fuel cooled for 8.5 years.

Hydride Re-orientation

Referring to Joe Rashid's presentation (Slide entitled "Hydrogen Precipitation" with data points developed by Kim Gruss, provided by Chuck Interrante and fitted by Joe Rashid), the maximum amount that can re-precipitate in the form of radial hydrides starting from 400°C is a function of hoop stress:

- An initial hoop stress of 200 MPa results in a maximum of 82 ppm of hydrogen that would be susceptible to re-precipitate as radial hydrides

- An initial hoop stress of less than 145 MPa results in no hydrogen that would be susceptible to re-precipitate as radial hydrides[1]

Although it can be argued that the data fit is uncertain[2], it is worth noting that the fraction of hydrogen re-precipitating as radial hydrides is likely to be just a few percent in the absence of repeated thermal cycling.[3] From this example, it can be concluded that the extent of hydride re-orientation is quite small at 400°C over a wide range of cladding hoop stress.

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[1] The latter was interpolated by noting that, upon cooling, hydrogen in solid solution will start re-precipitating when the cladding temperature reaches 335°C (see Albert Machiels' presentation, and more specifically, the section dealing with "Radial Hydrides").

[2] Rashid's fit gives, at 335°C, a threshold stress of ~130 MPa, below which hydrogen will re-precipitate in a circumferential direction only.

[3] See for example B.F. Kammenzind et al., "The Long-Range Migration of Hydrogen Through Zircaloy in Response to Tensile and Compressive Stress Gradients", ASTM STP 1354, Table 10 (page 226).

Starting from temperatures higher than 400°C requires the following considerations:

- Changes in the material microstructure can substantially increase the susceptibility for hydrogen to re-precipitate in the form of radial hydrides. Based on a limited amount of experimental information generated by Electricité de France on unirradiated cladding with 233 and 272 ppm of hydrogen, a 470°C/240-hour heat treatment does not appear to negatively impact the cladding microstructure with regard to hydride orientation, while a 520°C/24-hour heat treatment definitely does so.

- The amount of hydrogen available for re-precipitation increases with increasing temperatures. For example, if we assume that the initial storage temperature is still 400°C, as in the case illustrated in Rashid's presentation, but with a superimposed temperature transient to 470°C[4], then, for the same initial storage conditions of a hoop stress of 200 MPa and a temperature of 400°C, the maximum amount of hydrogen available for re-precipitation is 235 ppm instead of 82 ppm. In addition, since re-precipitation begins, in this case, as soon as the temperature drops below ~405°C, the fraction of hydrogen ending up in the form of radial hydrides will be somewhat higher. This is due to the fact that, when the cladding temperature drops from 405°C to 335°C, re-precipitation occurs under slightly higher hoop stress conditions.

From these considerations, it can be concluded that hydride re-orientation can be kept at a low to moderate level by defining an upper cladding temperature somewhere in the 400-470°C range in the absence of repeated thermal cycling.

Thermal Cycling

Theoretical Considerations

It has been widely observed and reported that repeated heatup/cooldown cycles, or thermal cycling, can enhance the amount of hydrogen that eventually re-precipitates in the form of radial hydrides.

For a given material, the amount of hydrogen that may re-precipitate as radial hydrides is a function of the number of thermal cycles, upper temperature, difference between the upper and lower temperature, and magnitude of applied stress. Other factors that may have an impact include the hold times at the upper and lower temperatures, because they affect the kinetics of hydride dissolution and hydrogen re-distribution.

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[4] For example, resulting from vacuum drying.

The upper temperature and the difference in temperature between the lower and upper temperatures determine the amount of hydrides that goes back into solution during each cycle. This is illustrated by the following example:

An upper temperature of 400°C is assumed. Let us assume that the thermal cycling occurs between 400°C and respectively 340°C, 300°C, 280°C, 220°C, 160°C, and 100°C.

Using Kammenzind et al.'s results [Kammenzind et al., ASTM STP 1295, pp. 338-370], the solubility limit of hydrogen is 210 ppm at 400°C.

Upon cooling, the amounts of hydrogen present in solid solution at the lower temperature, and the amount of cycled hydrogen (hydrogen re-dissolved and re-precipitated at each cycle) are:

Lower Temperature	Hydrogen in Solid Solution	Cycled Hydrogen
340°C	210 ppm	0 ppm
300°C	154 ppm	56 ppm
280°C	127 ppm	83 ppm
220°C	65 ppm	145 ppm
160°C	28 ppm	182 ppm
100°C	9 ppm	201 ppm

When the hoop stress is above the threshold stress for re-orientation, a fraction of the "cycled hydrogen" will re-precipitate as radial hydride following the completion of the first cycle.

Upon re-heating at the start of the second cycle, both types of hydrides (circumferential and radial) will undergo some re-dissolution to bring the amount of hydrogen in solid solution back to 210 ppm at 400°C. For example, if cycling occcurs between 280°C and 400°C, both types of hydrides will re-dissolve upon heating to put 83 ppm of hydrogen back into solid solution.

Taking into account the effect of stress on the hydride dissolution solvus, and using the equation on page 222 of the paper by Kammenzind et al. [ASTM STP 1354, pp.196-233], the equilibrium concentration of hydrogen at 400°C is a function of the applied stress as follows:

Applied Stress [MPa]	Equilibrium Concentration [ppm]
0	210
145	200
200	197

Therefore, if we assume that the radial hydrides are subject to a hoop stress of 200 MPa at 400°C,[5] equilibrium conditions will dictate that dissolution of radial hydrides will stop when the hydrogen concentration in their vicinity is equal to 197 ppm, while for circumferential hydrides, their dissolution will stop only when the hydrogen concentration in their vicinity reaches 210 ppm.[6] Moreover, hydrogen concentrations will tend to equilibrate in the material because of the classic diffusion process (Fick's law) driven by concentrations gradients. Movement of hydrogen away from the higher-concentration zones adjacent to the circumferential hydrides to the lower-concentration zones adjacent to the radial hydrides will occur until a uniform solid-solution concentration of 210 ppm is obtained throughout the material. Therefore, everything else being equal, under the conditions of interest to spent-fuel dry storage, the circumferential hydrides will dissolve to a greater extent than the radial hydrides: first, as a result of the effect of stress on the hydride dissolution solvus, and second as a result of diffusion of hydrogen from the vicinity of the circumferential hydrides to the vicinity of the radial hydrides driven by the aforementioned concentration gradient.

Upon cooling at the end of the second cycle, hydrogen will re-precipitate as circumferential and radial hydrides, the distribution between these two being mostly a function of temperature and the stress distribution in the cladding.

Therefore, it can be seen that repeated thermal cycling eventually may lead to the formation of significant amounts of radial hydrides, when the conditions for re-orientation (i.e., temperature, magnitude of stress, susceptibility of material to re-orientation) are met.

Practical implications

If we assume that the reference high-burnup cladding has an average concentration in hydrogen equal to 600 ppm[7], limiting the amount of cycled hydrogen to less than 10%, or less than 60 ppm, would limit the temperature swing to 100°C, or less, taking 400°C as the upper temperature limit. In other words, thermal cycling would be conservatively limited to a few cycles in the range between 400°C and 300°C.

Given that peak cladding temperatures are experienced by a limited fraction of the cladding in a dry, inert container, the low propensity for re-orientation when peak cladding temperatures are limited to 400°C, and the limited amount of hydrogen in play when the difference in temperature is ≤100°C, it can be inferred from the considerations presented above that re-orientation would

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[5] This is a rather high value for the hoop stress, which implies heavy corrosion, or the presence of hydride lenses, or both.

[6] This assumes that the circumferential hydrides are stress free.

[7] The choice of 600 ppm is obtained by choosing a PWR spent fuel clad in Zircaloy-4, at an elevation that is heavily corroded (~100 μm in oxide thickness), and averaging its total hydrogen content over the cross section of the cladding tube at that elevation.

be kept to a minimum even after a small number (nominally up to five) of such thermal cycles. This would be consistent with the experimental results reported, for examples, by Kammenzind [ASTM STP 1354, pp. 196-233] and Simpson et al. [ASTM STP 633, pp. 630-642].

If the threshold hoop stresses are sufficiently high, the effect of thermal cycling will be expected to become more pronounced as the upper temperature increases (i.e., >400°C), and less pronounced as the upper temperature decreases (i.e., <400°C). The effect of thermal cycling will be expected to become more pronounced as the difference between the upper and lower temperatures increases (i.e., >100°C), and less pronounced as the difference between the upper and lower temperatures decreases (i.e., <100°C). When the difference is less than ~65°C, there will not be any thermal cycling effect.

Temperature Limits

Considering that the fraction of the spent fuel cladding that experiences a temperature close to the peak cladding temperature is limited due to the radial and axial temperature gradients that exist within the canister or cask, the recommendation for an upper temperature limit would be as follows:

If the revised guidance adopts a single temperature limit, i.e., maximum temperature during drying as well as initial storage temperature, then 400°C represent an appropriate limit to minimize the potential for excessive creep strain.

If the revised guidance continues the present regulatory practice, i.e., (1) an initial storage peak cladding temperature, and (2) a second, higher temperature limit for short-term events such as drying, then:

- For (1), a temperature of 400°C, as discussed, for the initial storage peak cladding temperature, and
- For (2), a temperature between 400°C and 470°C. A likely temperature limit would probably be closer to the upper limit (470°C) than the lower limit (400°C). However, at this time, this last statement should be viewed as being of a more speculative nature.

2. Manufacturing of Cladding for PWR and BWR Applications

For PWR applications, Zircaloy-4 has been extensively used. It is still being used today, although newer, more corrosion resistant claddings, such as Zirlo™ and M5, will likely become the reference claddings for PWR fuels for all reloads in future years.

For PWRs, Zircaloy-4 in the stress relieved annealed (SRA) condition is characterized by very elongated grains (shaped like flat pancakes) lying in the circumferential-longitudinal plane. In addition, the very sharp radial texture of typical SRA fuel cladding results in a very low proportion of basal poles in the circumferential direction. These features are conducive to precipitation of the hydrides in the desired circumferential direction.

For BWR applications, Zircaloy-2 in the recrystallized annealed condition (RXA) is the reference condition. For recrystallized cladding, the grains are equiaxed. In addition, increased resistance to corrosion under BWR conditions can be obtained by introducing a beta quench[8] step near the end of the cold reduction process during tube fabrication. Beta quenching results in a random texture. Although the final tube fabrication step(s) will restore a radial texture, the combination of RXA (equiaxed grains) and late beta quench (effect on texture) makes this type of cladding more susceptible to hydride re-orientation.

It should be noted, however, that cladding hoop stress levels in BWR fuels are typically a factor of two to three lower than in PWR fuels. Therefore, for a given temperature, the lower hoop stress levels largely mitigate the higher susceptibility of BWR cladding to hydride re-orientation.

3. Cladding Integrity During Hypothetical Accident Conditions

As discussed at the end of the July 10 meeting, the need for predicting cladding integrity under hypothetical accident conditions can be debated on the basis of the existing regulatory requirements, how these regulatory requirements are met, and whether cladding integrity needs to be formally considered. Regulations applicable to hypothetical accidents include consideration of:

- Criticality for both storage and transportation
- Confinement for both storage and transportation
- Shielding for transportation.

For criticality (§72.124 and §71.55), the bounding configuration is likely to be the intact fuel assemblies. For confinement, the integrity of the confinement barriers is key for assessing the dose at the nearest boundary of the controlled area (<5 rem per §72.106), or the escape of krypton-85 (<10 A_2 in a week per §71.51). For shielding (§71.73), the external radiation dose rate is specified as not exceeding 1 rem/h at 1 m from the external surface of the package.

Under hypothetical accident conditions, loss of cladding integrity would likely lead to some relocation of fuel debris closer to the container wall. As far as heat transfer is concerned, the

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[8] Beta quenching is a term used to denote a process where the Zircaloy is heated above 1000°C to an all-beta phase structure, and then rapidly cooled, usually by a water quench.

least favorable configuration is likely to be the intact fuel assemblies given that, for this geometry, heat needs to be transferred from the center of the container toward its periphery. Relocation of any amount of fuel closer to the periphery would likely lead to a cooler geometry. For shielding, the same argument cannot be advanced. However, self-shielding is an important feature in shielding calculations, and it remains applicable whether the fuel assemblies remain intact, or whether some relocation occurred. Given the difference in radiation standards between §71.47 and §71.51, and the consideration of self-shielding, reconfiguration of the fuel is unlikely to violate the requirements of §71.51 when the requirements of §71.47 are met to start with.[9]

The assessment of cladding integrity under hypothetical accident conditions would have benefits with regard to the following issues:

- Provide more realistic values than those specified in ISG-5, where 100% rod breakage fraction for the confinement evaluation is assumed for design basis accident and extreme natural phenomena
- Provide a sound technical basis for specifying an upper temperature limit for short-term transients.

With regard to the latter, much of the discussion at the July 10 meeting focused on the formation and potential impact of radial hydrides as they relate to Failure Mode III.[10] Generally, it was concluded that temperature transients are not beneficial when Mode III, and Mode III only, is considered. This conclusion provides additional support for a 400°C temperature limit, as discussed previously. However, temperature transients can be beneficial in terms of restoring desirable material property characteristics when only Modes I and II are considered. Therefore, taking all three potential failure modes into account, a different result, i.e., a temperature higher than 400°C, would likely be derived.

This higher temperature, applicable to short-term events only, could, in principle, be determined by modeling and assessing the relative importance of the three failure modes including the beneficial/deleterious effects of a post-irradiation "heat treatment". Mode III would be expected to be negatively impacted; however, radial hydrides could be of limited concern depending on their eventual size and their ability to respond to impact loads.[11] Modes I and II would be expected to be positively impacted, because of the improved ductility of the cladding under impact loading.

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[9] This would have to be verified, of course.

[10] Please refer to Joe Rashid's presentation for the definition of Mode III.

[11] See, for example, K. Kese's report (SKI Report 98:32) that documents the retention of ductile behavior of Zircaloy with radial hydrides in the temperature range of interest to hypothetical accident conditions.

Therefore, there may be mutual interest in pursuing an approach where the models and materials properties in the report SAND-2406 would be updated. This would then allow performing parametric analyses of the effects of a temperature transient on the cladding response under hypothetical accident conditions. A potential result from such work would be the definition of a defensible upper temperature limit for short-term events, such as drying, as well as providing a basis for more realistic source term estimates.

4. Summary

Assuming that the revised guidance adopts a single temperature limit, we recommend consideration of 400°C, with no imposition of a hoop stress limit.[12] Under these conditions, the potential for any hydride re-orientation as well as any annealing is limited, and significant changes in cladding mechanical properties are not expected. Excessive deformation of the cladding due to thermal creep is prevented.

With regard to future work relevant to the response of high-burnup fuel cladding under hypothetical accident conditions, we propose re-visiting some of the evaluations reported in SAND-2406 with the objectives of assessing the probability of rod breakage under hypothetical accident conditions, including the effects of cladding experiencing temperatures higher than 400°C during short-term transients.

Thank you for the opportunity to provide some supplemental information.

Sincerely,

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Sr. Technical Manager

c: W. Hodges (NRC, SFPO)
J. Rashid (ANATECH)
A. Nelson (NEI)
L. Hendricks (NEI)

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[12] Imposing a temperature <u>and</u> a hoop stress limit is unnecessary given the interdependence between these two variables.