From: George Hubbard NRR
To: Glenn Kelly, Robert Palla NRR
Date: Thu, Aug 24, 2000 8:06 AM
Subject: Fwd: Spent Fuel Temp

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From: Charles Tinkler
To: George Hubbard, Joseph Staudenmeier
Date: Thu, Aug 24, 2000 7:46 AM
Subject: Spent Fuel Temp

Attached is a draft of my writeup on temperature criteria.

this time it should really be attached

CC: Farouk Eltawila, Jason Schaperow, John Flack, Timothy Collins

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The engineering analyses performed to address spent fuel pool performance during various accidents have, in the past, used a temperature criterion to evaluate the potential for significant fuel damage. This temperature was intended as an acceptance criterion beyond which one would expect the onset of significant, global, fuel damage and substantial release of fission products (e.g., 50-100% of inventory of volatiles) associated with such damage. Further, the temperature criterion cited (generally about 900°C) has been selected on the basis that it represented a threshold for self sustained oxidation (Ref. 1) of cladding in air and on that basis it has been argued that if cooling of the spent fuel could limit fuel temperatures in equilibrium below this threshold then large releases of fission products need not be considered. Self sustaining reaction in this sense means the reaction rate and thus heat generation rate is sufficient, to roughly balance heat losses for given cooling mechanisms, resulting in an isothermal condition. Once the fuel temperature exceeds this threshold temperature (alternatively identified as an ignition or autoignition temperature) it was presumed that subsequent heat up and further increases in reaction rates would be escalating and rapid and that serious fuel damage would ensue. The temperature escalation associated with oxidation in this regime would not be balanced by any reasonable cooling afforded by natural circulation of air. While it was not expected that fission product releases associated with core melt accidents would immediately emerge at this temperature (based on reactor research in various steam and hydrogen environments) it was recognized that the time window for subsequent fuel heating would be relatively small once oxidation escalated. This also did not preclude gap type releases associated with fuel failures below the threshold temperature but these generally were not considered to be significant compared to the releases associated with higher fuel temperatures and significant fuel damage.

In the report, "Draft Final Technical Study of Spent Fuel Pool Accident Risk at Decommissioning Nuclear Power Plants", February 2000, the temperature criterion selected, 800°C, was used in two ways. First, it was used to determine the decay heat level and corresponding time at which heat generation and losses for complete and instantaneous draining of the pool would lead to heating of the fuel (to 800°C) after 10 hours. This time period would allow for the implementation of effective emergency response without the full compliment of regulatory requirements associated with operating reactors. Secondly, the temperature criterion was also used to evaluate the decay heat level and time ("critical decay time") at which heat generation and losses for a fully drained fuel pool would result in an equilibrium temperature of 800°C (typically this critical decay time has been on the order of 5 years) On that basis it was reasoned that since serious overheating of the fuel had not occurred, the fission product release associated with core melt need not be considered.

The NRC has received a number of comments related to the use of this temperature criterion and has reassessed the appropriateness of such a value for both its intended purposes. At the outset RES acknowledges that an ignition temperature, or more precisely in this case a temperature for incipient temperature escalation is dependent on heat generation and losses which in turn is dependent on system geometry and configuration. In fact much of the data on oxidation is produced in isothermal tests up to near the melting temperature of zirconium. In examining an appropriate criterion, it is useful to consider the range of available data including core degradation testing in steam environments since it is likely that many spent fuel pool accidents may involve some initial period during which steam kinetics controls the initial oxidation, heatup, and release of fission products. In various experimental programs around the world (e.g., PBF-SFD, ACRR, CORA, NSRR, PHEBUS and QUENCH) repeatable phenomena have been observed for the early phase of core degradation (in steam) which

proceeds initially at rates associated with decay heat (at levels characteristic of reactor accidents) until cladding oxidation becomes dominant and temperature escalation occurs. The point at which the escalation occurs, which does vary between tests, has been attributed to heat losses (Reference 2) characteristic of the facility and to the monoclinic to tetragonal phase change of ZrO_2 over a temperature range. The threshold at which temperature escalation occurred has been reported to vary from approximately 1100°C to 1600°C. In a CORA test performed with a lower initial heat up rate (to simulate reduced decay heat during shutdown conditions) it was reported that uncontrolled temperature escalation did not occur, raising the prospect that heating rate may be a factor. In more recent QUENCH tests (Quench 04 and 05) the effect of preoxidation was evaluated for its effect on hydrogen generation and temperature escalation. In Quench 04 temperature escalation was reported to occur at 1300°C; in Quench 05 with approximately 200μm preoxidation temperature escalation was reported to be delayed until the fuel rod temperature reached 1620°C.

Because of interest in air ingression phenomena for reactor accidents, recent severe accident research has also examined oxidation in air environments. Publication of results from the DRESSMAN and CODEX test programs (Reference 3) has provided much of the transient data on fuel rod and rod bundle behavior for air kinetics as well as data on fuel oxidation and volatility. Early studies of zirconium oxidation in air (References 4and5) were performed to compare isothermal oxidation and scaling of fresh samples to determine the influence of different atmospheres and materials as well as to examine potential for fire hazards. The general observation is that, at least at higher temperatures(>1000°C), the oxidation rate is higher in air than in steam. Another observation of the early studies was, under the same conditions, oxidation in an air environment produced an oxide layer or scale less protective than that for steam owing to the possible instability of a nitride layer beneath the outer oxide layer leading to scale cracking and a breakaway in the oxidation rate. The onset of this breakaway in the oxidation rate occurred at about 800°C after a time period of 10 hours in the studies performed by Evans et al(Ref. 4). As breakaway oxidation occurs the oxidation behavior observed no longer reflects a parabolic rate dependence but takes on a linear rate dependence. Also, at lower temperatures the kinetics of reaction indicate near cubic rate dependence thus the representation of the oxidation behavior at both high and low temperatures with a parabolic rate dependence may introduce unnecessary simplification and an understatement of the low temperature behavior. Breakaway scaling in an isothermal test may not translate to similar behavior under transient heatup conditions where initial oxidation occurs at lower temperatures and may involve steam oxidation. The presence of hydrides in the cladding may also increase the potential for exfoliation and a breakaway in the oxidation; the effect of this has, however, been seen more clearly in testing conducted with steam and high hydrogen concentrations.

Autoignition is known to occur in zirconium alloys and zirconium hydride, especially when clean metal at high temperature (800°C) is suddenly exposed to air (Reference 8). The temperature of ignition is also highly dependent on the surface area to volume ratio. Generally, the mechanism of abrupt exposure of hot zircalloy metal to an air environment is not applicable to spent fuel pool accidents where fuel rods are covered with a relatively thick oxide layer. However, if there is clad failure by ballooning and burst (over a temperature range of 700-850°C) there is potential for hot oxide-free metal to be abruptly exposed to air. In this instance though, the surface area to volume ratio will be small and it is considered that the likelihood for any localized ignition to propagate is small.
In the CODEX tests annular cladded fuel (in a 9 rod bundle) were heated with an inner tungsten heater rod to examine fuel degradation, with preoxidized cladding, in an air environment.

Oxidation kinetics were evaluated as well as the oxidation of the fuel. In the CODEX AIT -1 test the early phase of the test involved creating a preoxidation using an argon-oxygen mixture. The intent was to achieve a controlled preoxidation at a temperature of 900-950°C, but it was reported (Ref. 3) that preoxidation was started at a slightly higher temperature than planned. What subsequently occurred was an uncontrollable temperature escalation up to approximately 2200°C before it was cooled with cold argon flow. After restabilization of the rods at 900°C air injection was started, electrical heatup commenced, and a second temperature escalation occurred. In the CODEX AIT-2 test, designed to proceed to a more damaged state, the preoxidation phase was conducted in an argon/steam mixture at 820°C and 950°C. (a malfunction occurred during the preoxidation phase resulting in the admission of a small air flow as well). No temperature escalation was seen during the preoxidation phase. Following the restabilization of the fuel rods, a linear power increase was started and a temperature excursion subsequently occurred.

In addition to examining relevant test data RES also looked at determining a temperature based threshold for temperature escalation in an air environment by determining equivalent heat generation from steam transient tests. In this exercise we posited that at equivalent heat generation rates, i.e., accommodating different reaction rates and different heats of reaction for air and steam we should be able to predict the corresponding temperature for escalation in air based on temperature escalations seen in severe fuel damage tests conducted in steam. Using this approach, the heat generation rate was estimated, assuming parabolic kinetics, and and the following equation for a rate constant in air:

$$k_p = 52.67 \exp(-17597/T)$$

It was predicted that based on an escalation temperature of 1200°C in steam (observed in many of the steam tests) the equivalent heat generation rate in air would produce a temperature escalation at approximately 925°C. The above equation for air kinetics was identified in Reference 3 as the best fit for the CODEX AIT test data, i.e., it provided the best agreement to the temperature transient in the peak position. For steam kinetics, the rate equation used in MELCOR was selected for calculating the heat generation rate. The prediction of an escalation temperature in air using this approach seems to conform quite well with the observed behavior in the transient CODEX tests and lends further credence to the relative effect of oxidation in air with respect temperature escalation. The assumption of parabolic kinetics is routine in oxidation calculations and has been shown to provide a good match with a wide spectrum of experimental data even though, over select temperature ranges, deviations from that formulation have been observed. At temperatures above 900°C , the reaction rate in air is high, regardless of whether parabolic or linear kinetics is assumed at that point and distinguishing between the rates of escalation is unimportant for our purposes.

In assessing a temperature criterion for escalation of the oxidation process and subsequent temperature escalation it is necessary to reconsider the intended uses of the criterion: 1) to evaluate the decay time after which the fuel heatup, in the case of complete fuel uncovery, leads to reaching that temperature at 10 hours and 2) to evaluate the decay time after which the fuel heatup, in the case of complete uncovery will never exceed the temperature criterion.

On balance it appears that a reasonable criteria for the threshold of temperature escalation in an air environment is a value of approximately 900°C. This value is supported by both limited experimental data as well as by inference from the more abundant steam testing data. While

certain weight gain data indicate the onset of a break away in the oxidation rate at lower temperatures after a period of 10 hours this additional time period then exceeds the time interval for which the first use of the criterion is intended. With regard to the second use of the criterion, determination of the point at which severe fuel heatup is precluded, the onset of breakaway indicated in certain tests indicates that the temperature criterion should be lowered to 800°C. It is important to stress that, in both instances, the temperature criteria should be used together with a thermal-hydraulic analysis that considers heat generation (i.e., decay heat and zircalloy reactions) and heat losses. For the second use of the criterion, i.e., establishing a threshold for precluding escalation, the analysis must demonstrate that heat losses, through convection, conduction and radiation, are sufficient to stabilize the temperature at the value selected.

In the case of slow, complete draining of the pool or partial draining of the pool it is appropriate to consider use of a higher temperature criterion for escalation, perhaps as high as 1100 to 1200°C. This would be appropriate if the primary oxidation reaction was with steam. Such a temperature criterion is relevant for the first intended use of the criterion, determining the point at which the temperature is not exceeded for 10 hours, however it is not appropriate for use as a long term equilibrium temperature since over long intervals at such high temperature one might reasonably expect significant fission product releases.

In addition to comments on the selection of an ignition temperature the staff received comments related to the effect of intermetallic reactions and eutectic reactions. With respect to intermetallic reactions, the melting temperature of aluminum, which is a constituent in BORAL poison plates in some types of spent fuel storage racks, is approximately 640°C. Molten aluminum can dissolve stainless stell and zirconium in an exothermic reaction forming intermetallic compounds. In the spent fuel pool configuration , zircalloy cladding will be covered with an oxide layer and unless, significant fresh metal surface is exposed through exfoliation there will be no opportunity to interract metallic zircalloy with aluminum (which similarly will be oxidized). Aluminum and steel will form an intermetallic compound at a temperature of 1150°C, (Ref. 5) which is above the temperature criterion selected for fuel damage.

Besides intermetallic compounds, eutectic reactions may take place between pairs of various reactor materials, e.g., Zr-Inconel (937°C), Zr-steel (937°C), Zr-Ag-In-Cd (1200°C), Zr-B_4C (1627°C), steel-B_4C (1150°C), etc. (Ref. 6). Consideration of eutectics and intermetallics is important from the standpoint of heat addition as well as assuring the structural integrity of the storage racks and maintaining a coolable configuration. Noting the eutectic and intermetallic reaction temperatures, however it does not appear that formation of these compounds imposes any additional temperature limit on the degradation of cladding in an air environment.

Since the temperature criterion is also a surrogate of sorts for the subsequent release of fission products it is useful to consider the temperature threshold versus temperatures at which cladding may fail and fission products be released. Cladding is likely to fail by ballooning and burst in the temperature rang of 700-850°C, resulting in the release of fission products and fuel fines. At burst, clean Zircalloy metal will also be exposed, leading to an increase in oxidation although the total amount of metal involved will be limited. Creep failure of the cladding at or above 600°C is also a possibility. This temperature limit is roughly associated with the 10 hour creep rupture time (565°C) which has been used as a regulatory limit. While failure of the cladding at these lower temperatures will lead to fission product release, such release is considerably smaller than that assumed for the cases where the temperature criterion is

exceeded and significant fuel heatup and damage occurs. . Low temperature cladding failures might be expected to produce releases similar to those associated with dry cask accident conditions as represented in Interim Staff Guidance (ISG)-5. This NRC guidance document prescribes release fractions for failed fuel ($2x10^{-4}$ for cesium, ruthenium and $3x10^{-5}$ for fuel fines). Use of these release fractions would reduce the offsite consequences dramatically from the fuel melt cases, early fatalities would be eliminated and latent cancer fatalities would be reduced by a factor of 100. As the temperature limit is increases from 600°C to 900°C there is some reason to believe that ruthenium releases would be increased based on ORNL test data from unclad pellets. Canadian data indicate though, that in the case of clad fuel the ruthenium release did not commence until virtually all of the cladding had oxidized, by this point it might be surmised that the fuel configuration would be more closely resembling a debris bed than intact fuel rods. Selection of a temperature criterion for fuel pool damage also depends on the intended use, i.e., whether it is intended as the criterion for the 10 hour delay before the onset of fission product release or whether it is being used as a threshold for long term fission product release. If the criteria is being used to judge when 10 hours are available for evacuation then it may be argued that a higher temperature could be adopted, one associated with the significant release of fission products,1200°C, since the release of fission products at lower temperatures will likely be small. However, in air it may be that the oxidation rate above 900°C is sufficient to reduce the additional time gained to reach 1200°C to a relatively small amount. Selection of a temperature criterion for long term fuel pool integrity needs to consider that ruthenium release rates, in air, become significant at approximately 800°C, based on the data of Parker et al. (Ref. 7).

Selection of an acceptance criterion for precluding significant offsite release, after roughly 5 years, should also consider that ruthenium with a 1 year half life will be substantially decayed and that at 5 years cesium (and perhaps fuel fines such as plutonium) will dominate the dose calculation. For these reasons RES believes that the long term viability of the pool, in a completely drained condition (air environment), if it concerns time periods of approximately 5 years pool degradation should be assessed for a temperature of approximately 800°C. Again, an analysis needs to be performed to demonstrate that at that temperature an equilibrium condition can be established. While this would result in an offsite release there would be substantial time available to take corrective action after a 5 year decay time for the most recently loaded fuel. If shorter decay time periods are proposed for achieving the long term equilibrium temperature criterion then the impact of ruthenium releases would dictate reconsideration of this value.

In summary, we conclude that for assessing the onset of fission product release under transient conditions (to establish the critical decay time for determining availability of 10 hours to evacuate) it is acceptable to use a temperature of 900°C if fuel and cladding oxidation occurs in air. If steam kinetics dominate the transient heatup case, as it would in many boildown and drain down scenarios, then a suitable temperature criterion would be around 1200°C. For establishing long term equilibrium conditions for fuel pool integrity during spent fuel pool accidents which preclude significant fission product release it is necessary to limit temperatures to values of 600°C to 800°C. If the critical decay time is sufficiently long (>5 yrs) that ruthenium inventories have substantially decayed then it would be appropriate to consider the use of a higher temperature, 800°C, otherwise fission product releases should be assumed to commence at 600°C. These cases are marked by substantial time for corrective action to restore cooling and prevent smaller gap type releases associated with early cladding failures.

The degradation of fuel during spent fuel pool accidents is an area of uncertainty since most research on severe fuel degradation has focused on reactor accidents in steam environments. Because of this uncertainty we have tended to rely on the selection of conservative criterion for predicting the global behavior of the spent fuel pool. It is our recommendation that the modeling of spent fuel pool accidents be performed with codes capable of calculating the heat generation and losses associated with the range of accidents including phenomena associated with both water boiloff and air circulation. Further, the calculation of critical decay times for establishing both the validity of ad hoc evacuation and precluding fission product release must also include consideration of the exothermic energy of reactions (i.e., reactions with air and steam) with cladding or alternatively demonstrate that such energy contribution is negligible in comparison to decay heat at that point. Severe accident codes, such as MELCOR, developed for modeling the degradation of reactor cores, would seem to be a reasonable approach for analysis of integral behavior and would possess the general capabilities for modeling liquid levels and vapor generation, air circulation, cladding oxidation and fission product release. Use of a severe accident code also facilitates the use of self consistent modeling and assumptions for the analysis. The proper calculation of fission product releases depends in large part on the prediction of thermal hydraulic conditions. More detailed CFD modeling would improve the calculation of boundary conditions for air circulation and could be used in conjunction with integral codes to better evaluate convective cooling. The kinetics of cladding reactions should be confirmed with experiments designed to simulate the range of conditions of interest under steady state and transient heating. The experimental database on ruthenium releases under conditions applicable to spent fuel pool accidents is inadequate and we are currently extrapolating data from conditions which tend to maximize such releases.

While there is uncertainty in the analysis of spent fuel degradation, especially for the conditions of air ingression, it is also true that elements of the analysis contain conservatism. The assumption of 75-100% release of ruthenium initiated at lower temperatures is based in large part on tests with bare fuel pellets, testing of cladded fuel indicates that the cladding acts as a getter of oxygen limiting release of ruthenium until virtually all of the cladding has oxidized. Further, before significant ruthenium release occurs (in its more volatile oxide form) the surrounding fuel matrix must be oxidized. During transient heatup of a spent fuel pool with temperature escalation one would expect the ruthenium release to follow the oxidation of the cladding at which point the fuel would more likely resemble a debris bed (the seismic event may also contribute in that regard) limiting the release fraction. The competition between formation of hyperstoichiometric UO_2 and U_3O_8 may also limit the release fraction below that seen in the data. The use of a temperature criterion of 600°C to preclude significant fission product releases is conservative in that it is based on large part on data that discounts the effect of cladding to limit releases. The cladding failures at low temperatures will still allow substantial retention of fuel fines and the presence of unoxidized zircalloy will prevent formation of volatile forms of ruthenium. More prototypic experimental data on releases under these kinds of conditions may reveal that the onset of significant releases, especially ruthenium, would not occur under spent fuel pool accident conditions until fuel rod temperatures reached much higher temperatures associated with complete oxidation of the cladding.
Use of the hottest fuel assemblies to predict global release of fission products from the entire spent fuel inventory is a significant conservatism as well. Transient fuel damage testing indicates that at temperature escalation not all of the rod bundle undergoes rapid heating, cooler regions can avoid the oxidation transient. Prediction of the propagation of the temperature escalation to the cooler regions of the pool needs to be carefully examined to see if significant benefit can be gained, at a minimum it will lengthen the period of fission product

release reducing the concentration of activity in the plume of fission products for offsite consequence analysis.

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