

December 23, 2013

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Washington, DC 20555-0001

Attention: Rulemakings and Adjudications Staff

**PETITION FOR RULEMAKING**

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## **PETITION FOR RULEMAKING**

### **I. NEEDED REGULATIONS**

This petition for rulemaking is submitted pursuant to 10 C.F.R. § 2.802 by Mark Leyse of Atomic Safety Organization (“Petitioner”).

First, Petitioner requests that United States Nuclear Regulatory Commission (“NRC”) make a new regulation stipulating that the rates of energy release, hydrogen generation, and fuel cladding oxidation from the zirconium<sup>1</sup>-steam reaction be calculated by Spent Fuel Pool (“SFP”) Accident Evaluation Models, using data from multi-rod bundle (assembly) severe accident experiments.

Second, Petitioner requests that NRC make a new regulation stipulating that the rates of energy release (from both fuel cladding oxidation and fuel cladding nitriding), fuel cladding oxidation, and fuel cladding nitriding from the zirconium-air reaction be calculated by SFP Accident Evaluation Models, using data from multi-rod bundle (assembly) severe accident experiments, conducted with pre-oxidized fuel cladding.

(In an *April 2000* letter from Dana A. Powers, Chairman of Advisory Committee on Reactor Safeguards (“ACRS”), to Richard A. Meserve, Chairman of NRC, ACRS informed the NRC Staff “that nitrogen from air depleted of oxygen will interact exothermically with zircaloy cladding. The reaction of zirconium with nitrogen is exothermic by about 86,000 calories per mole of zirconium reacted. Because the heat required to raise zirconium from room temperature to melting is only about 18,000 calories per mole, the reaction enthalpy with nitrogen is ample.”<sup>2</sup> Nonetheless, as of

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<sup>1</sup> For consistency, this rulemaking petition uses the term “zirconium” to refer to all the various types of zirconium alloys that comprise fuel cladding. Zircaloy, ZIRLO, and M5 are particular types of zirconium alloy fuel cladding. In a SFP accident, the oxidation behavior of the different fuel cladding materials, with various zirconium alloys, would be similar because of their shared zirconium content.

<sup>2</sup> Dana A. Powers, Chairman of ACRS, Letter to Richard A. Meserve, Chairman of NRC, Regarding ACRS Recommendations for Improvements to the NRC Staff’s “Technical Study of

2013, the NRC MELCOR computer safety model—used to simulate SFP accidents—*does not* model the nitriding of zirconium fuel cladding.<sup>3)</sup>

Third, Petitioner requests that NRC make a new regulation stipulating that SFP Accident Evaluation Models be required to conservatively model nitrogen-induced breakaway oxidation behavior, which causes the protective zirconium dioxide layer on fuel cladding to degrade and oxidation rates to accelerate. Furthermore, SFP Accident Evaluation Models need to be required to conservatively model how the transition to nitrogen-induced breakaway oxidation occurs earlier with pre-oxidized fuel cladding than with fresh non-oxidized fuel cladding.

Fourth, Petitioner requests that NRC make a new regulation stipulating that licensees be required to use conservative SFP Accident Evaluation Models to perform annual SFP safety evaluations of: 1) postulated complete loss-of-coolant accident (“LOCA”) scenarios, 2) postulated partial LOCA scenarios, and 3) postulated boil-off accident scenarios.

## **II. STATEMENT OF PETITIONER’S INTEREST**

On March 15, 2007, Mark Leyse submitted a 10 C.F.R. § 2.802 petition for rulemaking (“PRM”), PRM-50-84,<sup>4</sup> to NRC. PRM-50-84 requested: 1) that NRC make new regulations to help ensure licensees’ compliance with 10 C.F.R. § 50.46(b) emergency core cooling systems (“ECCS”) acceptance criteria and 2) to amend Appendix K to Part 50—ECCS Evaluation Models I(A)(1), “The Initial Stored Energy in the Fuel.”

In 2008, NRC decided to consider the issues raised in PRM-50-84 in its rulemaking process.<sup>5</sup> And in 2009, NRC published “Performance-Based Emergency Core Cooling System Acceptance Criteria,” which gave advanced notice of a proposed

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Spent Fuel Pool Accident Risk at Decommissioning Nuclear Power Plants,” April 13, 2000, (ADAMS Accession No. ML003704532), pp. 3-4.

<sup>3</sup> K. C. Wagner, R. O. Gauntt, Sandia National Laboratories, Analysis and Modeling Division, “Mitigation of Spent Fuel Pool Loss-of-Coolant Inventory Accidents and Extension of Reference Plant Analyses to Other Spent Fuel Pools,” SAND1A Letter Report, Revision 2, November 2006, (ADAMS Accession No. ML120970086), p. 12.

<sup>4</sup> Mark Leyse, PRM-50-84, March 15, 2007 (ADAMS Accession No. ML070871368).

<sup>5</sup> Federal Register, Vol. 73, No. 228, “Mark Edward Leyse; Consideration of Petition in Rulemaking Process,” November 25, 2008, pp. 71564-71569.

rulemaking, addressing four objectives: the fourth being the issues raised in PRM-50-84.<sup>6</sup> In 2012, the NRC Commissioners voted unanimously to approve a proposed rulemaking—revisions to Section 50.46(b), which will become Section 50.46(c)—that was partly based on the safety issues Leyse raised in PRM-50-84.<sup>7</sup>

Leyse also coauthored a paper, “Considering the Thermal Resistance of Crud in LOCA Analysis,”<sup>8</sup> which was presented at the American Nuclear Society’s 2009 Winter Meeting.

### **III. BACKGROUND**

#### **III.A. Spent Fuel Pool Zirconium Fires in Steam and Air**

Regarding the initiation and consequences of a SFP zirconium fire, a September 2013 NRC document, NUREG-2157, states:

If cooling of the spent fuel were not reestablished, the fuel could heat up to temperatures on the order of 1,000°C (1,832°F). At this temperature, the spent fuel’s zirconium cladding would begin to react with steam or air in a highly exothermic chemical reaction called a runaway zirconium oxidation reaction or autocatalytic ignition. This accident scenario is often referred to as a “spent fuel pool zirconium fire.” Radioactive aerosols and vapors released from the damaged spent fuel could be carried throughout the spent fuel pool building and into the surrounding environment. This release could lead to exposures of the surrounding population and contamination of property (*e.g.*, land or structures) in the vicinity of the site.<sup>9</sup>

(Runaway zirconium oxidation would be more likely to commence in steam at local fuel-cladding temperatures between approximately 1000°C (1832°F) and 1200°C,

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<sup>6</sup> Federal Register, Vol. 74, No. 155, “Performance-Based Emergency Core Cooling System Acceptance Criteria,” August 13, 2009, pp. 40765-40776.

<sup>7</sup> NRC, Commission Voting Record, Decision Item: SECY-12-0034, Proposed Rulemaking—10 CFR 50.46(c): Emergency Core Cooling System Performance During Loss-of-Coolant Accidents (RIN 3150-AH42), January 7, 2013, (ADAMS Accession No. ML13008A368).

<sup>8</sup> Rui Hu, Mujid S. Kazimi, Mark Leyse, “Considering the Thermal Resistance of Crud in LOCA Analysis,” American Nuclear Society, 2009 Winter Meeting, Washington, D.C., November 15-19, 2009.2

<sup>9</sup> NRC, “Waste Confidence Generic Environmental Impact Statement: Draft Report for Comment,” NUREG-2157, September 2013, (ADAMS Accession No. ML13224A106), Appendix F, p. F-2.

(2192°F); and to commence in air at lower local fuel-cladding temperatures of 827°C (1520°F)<sup>10</sup> or 900°C (1652°F).<sup>11</sup>) (See Figure 1.)



**Figure 1. Zirconium Fuel Rod Simulators that Incurred Runaway Oxidation**

### **III.A.1. In a Spent Fuel Pool Accident, a Zirconium Fire Could Ignite in Steam if Fuel-Cladding Temperatures Reached 1000°C (1832°F)**

In either a partial SFP LOCA or station blackout (“SBO”) boil-off accident,<sup>12</sup> if the fuel assemblies were uncovered, the fuel cladding’s zirconium content would initially chemically react with the steam produced by the boiling water in the SFP.<sup>13</sup> And, in a SBO boil-off accident, if the water level in the SFP decreased to an elevation at approximately 66 percent of the height of the fuel assemblies, local fuel-cladding temperatures in the upper regions of the fuel assemblies would approach 2000°F

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<sup>10</sup> Zachary I. Franiewski *et al.*, Pennsylvania State University, “Spent Fuel Pool Analysis of a BWR-4 Fuel Bundle Under Loss of Coolant Conditions Using TRACE,” NucE431W S2013, May 2013, pp. iv, 2, 3, 8, 13.

<sup>11</sup> Allan S. Benjamin *et al.*, Sandia Laboratories, “Spent Fuel Heatup Following Loss of Water During Storage,” NUREG/CR-0649, March 1979, p. 47.

<sup>12</sup> A SBO is a complete loss of both grid-supplied and backup onsite alternating current power. The Fukushima Dai-ichi accident was a SBO accident that caused three reactor core meltdowns.

<sup>13</sup> Randall Gauntt *et al.*, Sandia National Laboratories, “Fukushima Daiichi Accident Study: Status as of April 2012,” SAND2012-6173, August 2012, p. 183.

(1093°C).<sup>14</sup> (If the fuel assemblies were rapidly uncovered in a partial SFP LOCA and the water level in the SFP decreased to an elevation at approximately 66 percent of the height of the fuel assemblies or lower, local fuel-cladding temperatures in the upper regions of the fuel assemblies would heat up to 2000°F (1093°C) or greater.) When local fuel cladding temperatures increased to approximately 1000°C (1832°F), the fuel cladding would incur significant additional heating from the exothermic (heat-generating) zirconium-steam reaction. The zirconium-steam reaction produces zirconium dioxide, hydrogen, and energy; the equation for the reaction is written as  $\text{Zr} + 2\text{H}_2\text{O} \rightarrow \text{ZrO}_2 + 2\text{H}_2 + \text{energy}$ . The energy (heat) generated by the reaction is approximately 6.45 megajoules per kilogram (kg) of Zr reacted.<sup>15</sup>

When zirconium reacts in steam it is possible for the reaction to become steam-starved, which occurs when hydrogen produced by the zirconium-steam reaction locally replaces steam (to varying degrees) at the surface of a fuel rod. This will mitigate oxidation rates or completely prevent oxidation.

The fuel-cladding outer surfaces of spent fuel assemblies are coated with varying thicknesses of zirconium dioxide layers (oxide layers). Oxide layers form on the fuel rods' cladding over the course of three or more years of operation in the reactor core, at elevated temperatures: typical BWR and PWR coolant temperatures are 540-550°F and 540-620°F, respectively.<sup>16</sup> There are also local crud (corrosion products) deposits on the outer surfaces of fuel cladding. Higher burnup fuel cladding typically has thicker oxide layers, and a higher hydrogen content. In a SFP accident the outer fuel-cladding oxide layer *can* function as a protective layer; the oxidation of zirconium at elevated temperatures *could* be “controlled by the diffusion of oxygen through the oxide [layer,

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<sup>14</sup> Electric Power Research Institute (“EPRI”), “Severe Accident Management Guidance Technical Basis Report,” Volume 2: “The Physics of Accident Progression,” 1025295, Appendix EE, p. EE-17.

<sup>15</sup> NRC, “Compendium of ECCS Research for Realistic LOCA Analysis,” NUREG-1230, 1988, (ADAMS Accession No. ML053490333), p. 8-2.

<sup>16</sup> International Atomic Energy Agency (“IAEA”), “Assessment and Management of Ageing of Major Nuclear Power Plant Components Important to Safety: BWR Pressure Vessels,” IAEA-TECDOC-1470, October 2005, p. 7; and IAEA, “Assessment and Management of Ageing of Major Nuclear Power Plant Components Important to Safety: PWR Pressure Vessels,” IAEA-TECDOC-1120, October 1999, p. 5.



with] the reaction rate [being] inversely proportional to the oxide thickness.”<sup>17</sup> However, if the cladding temperature increases, the temperature may become the dominating factor that drives the zirconium-oxidation reaction, causing a rapid cladding-temperature escalation.<sup>18</sup> (In the PHEBUS B9R-2 test—conducted with a pre-oxidized test bundle—oxide layers did not prevent a rapid fuel cladding temperature escalation from commencing *in steam* at a relatively low temperature: 1027°C (1880°F); PHEBUS B9R-2 is discussed in Section III.A.2.a.)

(In air, nitrogen-related breakaway oxidation behavior would cause the *protective* oxide layer to degrade at approximately 800°C; and oxidation rates would begin accelerating.<sup>19</sup>)

A SFP fire is *primarily a zirconium fire*: the *runaway* chemical reaction between zirconium and steam (or zirconium and air): *runaway zirconium oxidation*. Runaway zirconium oxidation causes *thermal runaway*, because zirconium oxidation is exothermic: the heat produced by the zirconium-steam reaction increases the local fuel-cladding temperature, which in turn increases the reaction rate, further increasing the local fuel-cladding temperature, and so on. Once runaway zirconium oxidation commences *in steam* (typically at local fuel-cladding temperatures between approximately 1000°C (1832°F) and 1200°C (2192°F), local fuel-cladding temperatures increase rapidly, leading to temperature increases of tens of degrees Fahrenheit per second. Hence, local fuel-cladding temperatures can escalate up to the point where zirconium melts—above 1816°C (3300°F)<sup>20</sup>—within a few minutes.

### **III.A.2. In a Spent Fuel Pool Accident, a Zirconium Fire Might Not Ignite in Steam if Fuel-Cladding Temperatures Reached 1000°C (1832°F) or Greater**

In either a partial SFP LOCA or SBO boil-off accident, it is possible that there would not be a temperature escalation, if local fuel-cladding temperatures increased to

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<sup>17</sup> S. Hagen, H. Malauschek, S. O. Peck, K.P. Wallenfels, “Temperature Escalation in PWR Fuel Rod simulator Bundles due to the Zircaloy-Steam Reaction: Test ESBU-1: Test Results Report,” KfK-3508, December 1983, p. 4.

<sup>18</sup> *Id.*, p. 5.

<sup>19</sup> C. Duriez, T. Dupont, B. Schmet, F. Enoch, “Zircaloy-4 and M5 High Temperature Oxidation and Nitriding in Air,” *Journal of Nuclear Materials* 380 (2008), pp. 30, 39, 40, 43, 44.

<sup>20</sup> NRC, “Feasibility Study of a Risk-Informed Alternative to 10 CFR 50.46, Appendix K, and GDC 35,” June 2001, (ADAMS Accession No: ML011800519), p. 3-1.

approximately 1000°C (1832°F), because the initial heatup rate of the fuel cladding would be very slow.

After the fuel cladding were uncovered it would *initially* heat up *very slowly*, in some scenarios, at local rates lower than 0.01°C/sec (0.018°F/sec);<sup>21</sup> in other scenarios, local heatup rates would be approximately 0.13°C/sec (0.23°F/sec).<sup>22</sup>

Regarding the zirconium-steam reaction in the reactor core, a 1999 paper, “Current Knowledge on Core Degradation Phenomena, a Review,” states that if the initial fuel-cladding temperature heat-up rate is 0.2°C/sec or lower, the heat-up rate will become 3.0°C/sec or lower if fuel-cladding temperatures reach 1200°C, because of the heat that would be contributed from the exothermic zirconium-steam reaction. The same paper also states that if the initial fuel-cladding temperature heat-up rate is 1.0°C/sec or greater, the heat-up rate will become 10.0°C/sec or greater if fuel-cladding temperatures reach 1200°C, because of the heat that would be contributed from the exothermic zirconium-steam reaction.<sup>23</sup>

An initial fuel-cladding temperature heat-up rate of 1°C/sec or greater means that there will be a thinner oxide thickness on the fuel cladding *for a particular temperature*; hence, oxidation rates become greater at fuel-cladding temperatures at which the exothermic zirconium-steam reaction contributes significant heat (6.45 megajoules per kg of Zr reacted).<sup>24</sup>

(It is noteworthy that if there were one or more criticality accidents in either a partial SFP LOCA or a SBO boil-off accident, after the fuel assemblies were uncovered, the heat generated from fission would cause rapid local fuel-cladding temperature increases.<sup>25</sup> Hence, it would be possible for initial heatup rates of the fuel cladding to be

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<sup>21</sup> Zachary I. Franiewski *et al.*, Pennsylvania State University, “Spent Fuel Pool Analysis of a BWR-4 Fuel Bundle Under Loss of Coolant Conditions Using TRACE,” p. 19.

<sup>22</sup> EPRI, “Severe Accident Management Guidance Technical Basis Report,” Volume 2: “The Physics of Accident Progression,” 1025295, Appendix EE, p. EE-10.

<sup>23</sup> P. Hofmann, “Current Knowledge on Core Degradation Phenomena, a Review,” *Journal of Nuclear Materials*, 270, 1999, p. 205.

<sup>24</sup> R. R. Hobbins, D. A. Petti, D. J. Osetek, and D. L. Hagrman, Idaho National Engineering Laboratory, EG&G Idaho, Inc., “Review of Experimental Results on LWR Core Melt Progression,” in NRC “Proceedings of the Eighteenth Water Reactor Safety Information Meeting,” NUREG/CP-0114, Vol. 2, 1990, (ADAMS Accession No. ML042250131), p. 7.

<sup>25</sup> Zachary I. Franiewski *et al.*, Pennsylvania State University, “Spent Fuel Pool Analysis of a BWR-4 Fuel Bundle Under Loss of Coolant Conditions Using TRACE,” pp. 1-2.

1.0°C/sec or greater. If fuel-cladding temperatures that had initial heatup rates of 1.0°C/sec or greater were to increase to between approximately 1000°C (1832°F) and 1200°C (2192°F) *in a steam environment*, runaway zirconium oxidation would most likely commence.)

Regarding the fact that the CORA experiments conducted with lower heat-up rates did not have temperature escalations, a 1996 European Commission report states:

The CORA experiments performed with lower heat-up rates demonstrated clearly that no temperature escalation took place. The chemical interaction energy evolved caused only an increased heat-up rate between [1200°C (2192°F)] and [1800°C (3272°F)] of about [1.0°C/sec (1.8°F/sec)]. The oxide layer which has formed on the cladding outer surface during heat-up delays the chemical interactions between Zircaloy and steam since the diffusion of oxygen through the ZrO<sub>2</sub> layer is the reaction rate-determining step. The Zircaloy will be almost completely oxidized, or at least converted into  $\alpha$ -Zr(O), before reaching the melting point of oxygen-poor (as-received) Zircaloy at about [1760°C (3200°F)]<sup>26,27</sup>.

The PHEBUS B9 test is an example of an experiment that did *not* have a rapid fuel-cladding temperature escalation that commenced at relatively low fuel-cladding temperatures, because *it had a low initial heatup rate*. In PHEBUS B9, conducted in December 1986, the initial fuel-cladding temperature heatup rate was 0.2°C/sec (0.36°F/sec); the test bundle heated up to 1547°C (2816°F) at a very slow rate, without a rapid fuel-cladding temperature escalation. At 1547°C (2816°F) a fuel-cladding temperature escalation of 5°C/sec commenced.<sup>28</sup>

The CORA-2 test is an example of an experiment that *had* a rapid fuel-cladding temperature escalation that commenced at relatively low fuel-cladding temperatures, because *it did not have a low initial heatup rate*. CORA-2 had an initial fuel-cladding temperature heatup rate of approximately 1.0°C/sec (1.8°F/sec). In CORA-2, a PWR-type test conducted with 25 fuel rods (16 heated and 9 unheated rods), an “uncontrolled

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<sup>26</sup> Zirconium melts at temperatures above 1816°C (3300°F). See NRC, “Feasibility Study of a Risk-Informed Alternative to 10 CFR 50.46, Appendix K, and GDC 35,” June 2001, (ADAMS Accession No: ML011800519), p. 3-1.

<sup>27</sup> T.J. Haste *et al.*, “In-Vessel Core Degradation in LWR Severe Accidents,” European Commission, Report EUR 16695 EN, 1996, p. 27.

<sup>28</sup> C. Gonnier *et al.*, “PHEBUS Severe Fuel Damage Program Main Experimental Results and Instrumentation Behavior,” Proceedings of the Seminar of the Phebus-FP (Fission Product) Project, Chateau Cadarache, St. Paul-Lez-Durance, France, June 5-7, 1991, p. 113.

temperature escalation started at about [1100°C (2012°F)].”<sup>29</sup> And the LOFT LP-FP-2 experiment is another example of an experiment that *had* a rapid fuel-cladding temperature escalation that commenced at relatively low fuel-cladding temperatures, because *it did not have a low initial heatup rate*. LOFT LP-FP-2, heated with “actual fission-product decay heating of the core,”<sup>30</sup> had an initial fuel-cladding temperature heatup rate of approximately 1.0°C/sec (1.8°F/sec).<sup>31</sup> In LOFT LP-FP-2, “[t]he first recorded and qualified rapid temperature rise associated with the rapid reaction between Zircaloy and water occurred at ...1400 K [1127°C (2060°F)] on a guide tube.” Hence, an analysis of LOFT LP-FP-2 “concluded from examination of the recorded temperatures that the oxidation of Zircaloy by steam becomes rapid at temperatures in excess of 1400 K (2060°F).”<sup>32</sup>

### **III.A.2.a. The PHEBUS B9R-2 Test had a Low Initial Heatup Rate and a Rapid Fuel-Cladding Temperature Escalation at Relatively Low Temperatures**

It needs to be clarified that even if there were a low initial heatup rate of the fuel cladding, it is still possible for a rapid fuel-cladding temperature escalation to commence *in steam* at relatively low fuel-cladding temperatures. The PHEBUS B9R-2 test is an example of an experiment that *had* an unexpected rapid fuel-cladding temperature escalation that commenced at relatively low fuel-cladding temperatures, even though *it had a low initial heatup rate*.

The PHEBUS B9R test was conducted in a light water reactor—as part of the PHEBUS severe fuel damage program—with an assembly of 21 UO<sub>2</sub> fuel rods. The B9R test was conducted in two parts: the B9R-1 test and the B9R-2 test.<sup>33</sup> A 1996 European

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<sup>29</sup> T.J. Haste *et al.*, “In-Vessel Core Degradation in LWR Severe Accidents,” European Commission, Report EUR 16695 EN, pp. 15, 16.

<sup>30</sup> S. R. Kinnersly, *et al.*, “In-Vessel Core Degradation in LWR Severe Accidents: A State of the Art Report to CSNI,” p. 3.23.

<sup>31</sup> T. J. Haste *et al.*, “Degraded Core Quench: A Status Report,” August 1996, p. 13.

<sup>32</sup> J. J. Pena, S. Enciso, F. Reventos, “Thermal-Hydraulic Post-Test Analysis of OECD LOFT LP-FP-2 Experiment,” International Agreement Report, NUREG/IA-0049, April 1992, (ADAMS Accession No: ML062840091), pp. 30, 33.

<sup>33</sup> G. Hache, R. Gonzalez, B. Adroguer, Institute for Protection and Nuclear Safety, “Status of ICARE Code Development and Assessment,” in NRC “Proceedings of the Twentieth Water Reactor Safety Information Meeting,” NUREG/CP-0126, Vol. 2, 1992, (ADAMS Accession No: ML042230126), p. 311.

Commission report states that the B9R-2 test had an unexpected fuel-cladding temperature escalation in the mid-bundle region; the highest temperature escalation rates were from 20°C/sec (36°F/sec) to 30°C/sec (54°F/sec).<sup>34</sup>

Discussing PHEBUS B9R-2, the 1996 European Commission report states:

The B9R-2 test (second part of B9R) illustrates the oxidation in different cladding conditions representative of a pre-oxidized and fractured state. This state results from a first oxidation phase (first part name B9R-1, of the B9R test) terminated by a rapid cooling-down phase. During B9R-2, an unexpected strong escalation of the oxidation of the remaining Zr occurred when the bundle flow injection was switched from helium to steam while the maximum clad temperature was equal to 1300 K [1027°C (1880°F)]. *The current oxidation model was not able to predict the strong heat-up rate observed* even taking into account the measured large clad deformation and the double-sided oxidation (final state of the cladding from macro-photographs).

*... No mechanistic model is currently available to account for enhanced oxidation of pre-oxidized and cracked cladding*<sup>35</sup> [emphasis added].

The fact that PHEBUS B9R-2 was conducted with a pre-oxidized test bundle makes its results particularly applicable to SFP fires. The results of PHEBUS B9R-2 indicate that it is unpredictable as to whether or not rapid fuel-cladding temperature escalations would commence *in steam*, in a SFP accident, at relatively low fuel-cladding temperatures.

Spent fuel rods would also be “pre-oxidized”: when high burnup (and other) fuel rods are discharged from the reactor core and loaded into the SFP, the fuel cladding can have local zirconium dioxide (ZrO<sub>2</sub>) “oxide” layers that are up to 100 µm thick (or greater); there can also be local crud layers on top of the oxide layers, which can sometimes also be up to 100 µm thick. And medium to high burnup fuel cladding typically has a “hydrogen concentration in the range of 100-1000 wppm [weight parts per

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<sup>34</sup> T.J. Haste *et al.*, “In-Vessel Core Degradation in LWR Severe Accidents,” European Commission, Report EUR 16695 EN, p. 33.

<sup>35</sup> *Id.*, p. 126.

million];” “[z]irconium-based alloys, in general, have a strong affinity for oxygen, nitrogen, and hydrogen...”<sup>36</sup>

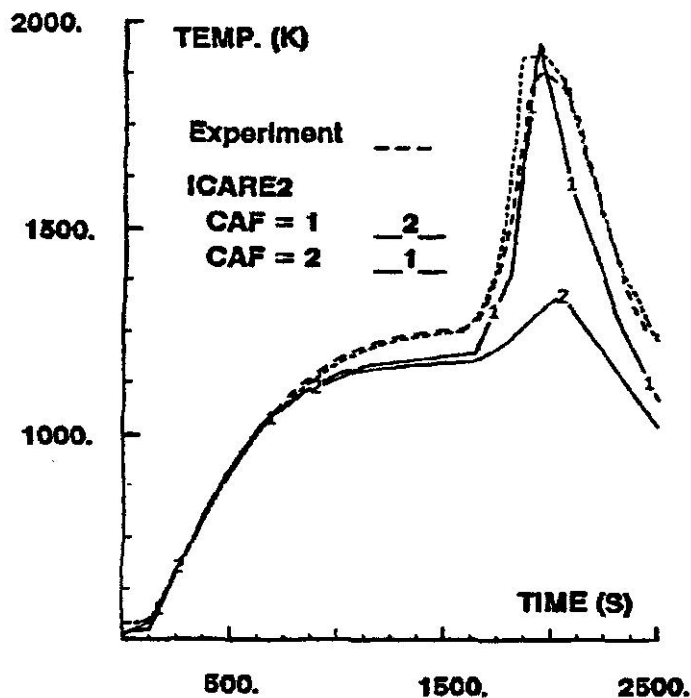
According to an October 2000 OECD Nuclear Energy Agency report, the initial heatup rate in PHEBUS B9R-2 was less than 0.1°C/sec up to 727°C (1340°F) (during the pure helium phase of the experiment).<sup>37</sup> However, according to a graph with a plot of fuel-cladding temperature values at the 0.6 meter “hot level” of the PHEBUS B9R-2 test bundle, the initial heatup rate in PHEBUS B9R-2 was approximately 1.0°C/sec up to 727°C (1340°F); however, the heatup rate decreases to lower than 0.2°C/sec between approximately 877°C (1610°F) and 1002°C (1835°F).<sup>38</sup> (See Figure 2.) As stated, the cladding-temperature escalation commenced at approximately 1027°C (1880°F).

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<sup>36</sup> K. Natesan, W.K. Soppet, Argonne National Laboratory, “Hydrogen Effects on Air Oxidation of Zirlo Alloy,” NUREG/CR-6851, October 2004, (ADAMS Accession No: ML042870061), p. iii, 3.

<sup>37</sup> OECD Nuclear Energy Agency, “In-Vessel Core Degradation Code Validation Matrix Update 1996-1999,” NEA/CSNI/R(2000)21, October 2000, p. 97.

<sup>38</sup> G. Hache, R. Gonzalez, B. Adroguer, Institute for Protection and Nuclear Safety, “Status of ICARE Code Development and Assessment,” in NRC “Proceedings of the Twentieth Water Reactor Safety Information Meeting,” NUREG/CP-0126, Vol. 2, 1992, (ADAMS Accession No: ML042230126), p. 312.



**Figure 2. Local Cladding Temperature vs. Time in the PHEBUS B9R-2 Test<sup>39</sup>**

(It is noteworthy that a September 2013 NRC document, NUREG-2157, states that if local fuel-cladding temperatures were to increase to approximately 1000°C (1832°F) in a SFP accident, a runaway zirconium oxidation reaction—a *SFP zirconium fire*—would commence *in steam*.<sup>40</sup> However, regarding zirconium fuel-cladding behavior *in steam*, in a reactor LOCA, in October 2012, NRC stated that “autocatalytic [zirconium oxidation] reactions have not occurred at temperatures less than 2200 degrees F;”<sup>41</sup> that is, runaway zirconium oxidation reactions have not commenced in experiments when fuel-cladding temperatures were lower than 1204.4°C (2200°F).

Hence, NRC claims that runaway zirconium oxidation would commence at 1000°C (1832°F) *in steam*, in SFP accidents, which would have low initial heatup rates (except in certain criticality accident scenarios). Nonetheless, NRC also claims that

<sup>39</sup> *Id.*

<sup>40</sup> NRC, “Waste Confidence Generic Environmental Impact Statement: Draft Report for Comment,” NUREG-2157, September 2013, (ADAMS Accession No. ML13224A106), Appendix F, p. F-2.

<sup>41</sup> NRC, “Draft Interim Review of PRM-50-93/95 Issues Related to Conservatism of 2200 degrees F, Metal-Water Reaction Rate Correlations, and ‘The Impression Left from [FLECHT] Run 9573’,” October 16, 2012, (ADAMS Accession No: ML12265A277), p. 2.

runaway zirconium oxidation would *not* commence below 1204.4°C (2200°F) *in steam*, in reactor LOCAs, which could have *high* initial heatup rates, exceeding 5.6°C/sec (10.0°F/sec).

Perhaps NRC’s statement regarding runaway zirconium oxidation *in steam*, in reactor LOCAs, is influenced by the fact that NRC requires the maximum fuel-cladding temperature in a postulated reactor LOCA to not exceed 2200°F—10 C.F.R. § 50.46(b)(1) peak fuel-cladding temperature limit. If NRC acknowledged that runaway zirconium oxidation *in steam* could commence in reactor LOCAs at fuel cladding temperatures below 2200°F, NRC might realize that it needed to lower its Section 50.46 peak fuel-cladding temperature limit.<sup>42)</sup>

### **III.A.3. In a Spent Fuel Pool Accident, a Zirconium Fire Would Most Likely Ignite in Air if Fuel-Cladding Temperatures Reached 900°C (1652°F) or Lower**

In either a partial SFP LOCA or a SBO boil-off accident, if the fuel assemblies were uncovered, the fuel cladding’s zirconium content would initially chemically react with the steam produced by the boiling water in the SFP. At some point, in a SBO boil-off accident, as more water boiled off and the water level decreased further (below the elevation at 66 percent of the height of the fuel assemblies), the fuel cladding would be exposed to local mixtures of steam and air. (If the fuel assemblies were rapidly uncovered in a partial SFP LOCA and the water level in the SFP decreased to an elevation at some point lower than 66 percent of the height of the fuel assemblies, the fuel cladding would be exposed to local mixtures of steam and air.) When zirconium is exposed to local mixtures of steam and air, the zirconium-oxygen reaction will dominate.<sup>43</sup> Then, as the water level dropped down even closer to the baseplates, the

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<sup>42</sup> Full disclosure: in November 2009, the author of this rulemaking petition submitted a rulemaking petition (PRM-50-93) to NRC, requesting that NRC revise 10 C.F.R. § 50.46(b)(1) to require that the calculated maximum fuel element cladding temperature, in a reactor LOCA, not exceed a limit based on data from multi-rod (assembly) severe fuel damage experiments. The author argued that data from multi-rod (assembly) severe fuel damage experiments (for example, the LOFT LP-FP-2 experiment) indicates that the current 10 C.F.R. § 50.46(b)(1) PCT limit of 2200°F is non-conservative.

<sup>43</sup> C. Bals *et al.*, “Modelling of Accelerated Cladding Degradation in Air for Severe Accident Codes,” The 3rd European Review Meeting on Severe Accident Research (ERMSAR-2008), Bulgaria, September 23-25, 2008, pp. 4, 5.



upper regions of the fuel assemblies would predominately be exposed to air. (After the fuel assemblies were uncovered there would be various local conditions; for example, there could be local steam starvation and local oxygen starvation.)

If there had been initial heatup rates that were very low (that is, if there had not been any criticality accidents that caused faster initial heatup rates) and a zirconium fire had not commenced *in steam*, a zirconium fire would most likely commence *in air*, provided water covered the baseplates at the lower end of the fuel assemblies. (If “water [is] above the base plate of the racks...the water at the bottom of the pool acts as a “plug,” which prevents cooling of the assemblies by natural air circulation.”<sup>44</sup>)

#### **III.A.4. Exothermic Reactions in Air: Zirconium Oxidation and Zirconium Nitriding**

Runaway zirconium oxidation commences *in air* at lower local fuel-cladding temperatures—827°C (1520°F)<sup>45</sup> or 900°C (1652°F)<sup>46</sup>—than it does in steam; and the zirconium-oxygen reaction in air produces approximately twice as much energy (per kg of Zr reacted) as the zirconium-steam reaction. The zirconium-oxygen reaction in air produces zirconium dioxide and energy; the equation for the reaction is written as  $\text{Zr} + \text{O}_2 \rightarrow \text{ZrO}_2 + \text{energy}$ . The energy (heat) generated by the reaction is approximately 12.0 megajoules per kg of Zr reacted.<sup>47</sup>

And the zirconium-nitrogen reaction produces approximately 30 percent of the quantity of energy (per kg of Zr reacted) produced by the zirconium-oxygen reaction in air. The zirconium-nitrogen reaction produces zirconium nitride and energy; the equation

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<sup>44</sup> Randall Gauntt *et al.*, Sandia National Laboratories, “Fukushima Daiichi Accident Study: Status as of April 2012,” SAND2012-6173, August 2012, p. 183.

<sup>45</sup> Zachary I. Franiewski *et al.*, Pennsylvania State University, “Spent Fuel Pool Analysis of a BWR-4 Fuel Bundle Under Loss of Coolant Conditions Using TRACE,” pp. iv, 2, 3, 8, 13.

<sup>46</sup> Allan S. Benjamin *et al.*, Sandia Laboratories, “Spent Fuel Heatup Following Loss of Water During Storage,” NUREG/CR-0649, March 1979, p. 47.

<sup>47</sup> National Research Council, Committee on the Safety and Security of Commercial Spent Nuclear Fuel Storage, “Safety and Security of Commercial Spent Nuclear Fuel Storage: Public Report,” 2005, p. 38.

for the reaction is written as  $\text{Zr} + 1/2\text{N}_2 \rightarrow \text{ZrN} + \text{energy}$ . The energy (heat) generated by the reaction is approximately 3.76 megajoules per kg of Zr reacted.<sup>48</sup>

In April 2000, the ACRS told the NRC Staff that “nitrogen from air depleted of oxygen will interact exothermically with zircaloy cladding. The reaction of zirconium with nitrogen is exothermic by about 86,000 calories per mole of zirconium reacted. Because the heat required to raise zirconium from room temperature to melting is only about 18,000 calories per mole, the reaction enthalpy with nitrogen is ample”<sup>49</sup> [emphasis added]. (A July 1987 NRC document, NUREG/CR-4982, states that the reaction of zirconium and nitrogen releases approximately 82,000 calories per mole of zirconium reacted.<sup>50</sup>)

An August 2012 SNL report, “Fukushima Daiichi Accident Study” states that “[i]f *inadequate* cooling is provided, then the cladding will heat up and will rapidly oxidize (*i.e.*, burn) and to a lesser extent, nitride (*i.e.*, combine with nitrogen if no oxygen or steam are available). *Since the oxidation and nitride processes are exothermic*, the fuel rods could heat to melting conditions and structurally degrade”<sup>51</sup> [emphasis added].

### **III.A.5. Nitrogen Accelerates the Oxidation and Degradation of Zirconium Fuel-Cladding in Air**

The nitrogen gas (in air) affects the oxidation of zirconium in air.<sup>52</sup> The presence of nitrogen accelerates the oxidation (burning) and degradation of zirconium fuel-cladding

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<sup>48</sup> V. L. Sailor *et al.*, Brookhaven National Laboratory, “Severe Accidents in Spent Fuel Pools in Support of Generic Safety Issue 82,” NUREG/CR-4982, July 1987, p. 109.

<sup>49</sup> Dana A. Powers, Chairman of ACRS, Letter to Richard A. Meserve, Chairman of NRC, Regarding ACRS Recommendations for Improvements to the NRC Staff’s “Technical Study of Spent Fuel Pool Accident Risk at Decommissioning Nuclear Power Plants,” April 13, 2000, (ADAMS Accession No. ML003704532), pp. 3-4.

<sup>50</sup> V. L. Sailor *et al.*, “Severe Accidents in Spent Fuel Pools in Support of Generic Safety Issue 82,” NUREG/CR-4982, p. 109.

<sup>51</sup> Randall Gauntt *et al.*, Sandia National Laboratories, “Fukushima Daiichi Accident Study: Status as of April 2012,” SAND2012-6173, August 2012, p. 183.

<sup>52</sup> K. C. Wagner, R. O. Gauntt, Sandia National Laboratories, Analysis and Modeling Division, “Mitigation of Spent Fuel Pool Loss-of-Coolant Inventory Accidents and Extension of Reference Plant Analyses to Other Spent Fuel Pools,” SAND1A Letter Report, Revision 2, November 2006, (ADAMS Accession No. ML120970086), p. 12; and L. Fernandez-Moguel, J. Birchley, European MELCOR User’s Group, “PSI air oxidation model in MELCOR: Part 2: Analysis of experiments and model assessment,” Stockholm, May 2013, which states: “Neither MELCOR nor SCDAP [a severe accident computer safety model] are able to predict a nitride reaction.”

in air,<sup>53</sup> which would affect the progression and severity of a SFP accident, including radioactive releases, “most notabl[y] ruthenium.”<sup>54</sup> (“Ruthenium has a biological effectiveness equivalent to that of Iodine-131;”<sup>55</sup> Ruthenium-106 has half-life of 373.6 days.)

A 2010 Journal of Nuclear Materials paper observes that “[t]he complexity of air oxidation of Zircaloy arises out of the simultaneous oxidation and nitriding processes.”<sup>56</sup> And a May 2013 report, “Results of the QUENCH-16 Bundle Experiment on Air Ingress,” discusses experimental data demonstrating that porous nitrides form inside oxide layers *under local or full oxygen-starvation conditions*.<sup>57</sup> (When zirconium reacts in air it is possible for the reaction to become oxygen-starved; however, if zirconium is locally oxygen-starved in air, nitrogen will react with it.) The porous, degraded condition of an oxide layer facilitates accelerated oxidation rates if additional oxygen becomes *locally* available; and any additional oxygen will react with the zirconium nitride (ZrN) within an existing oxide layer and form zirconium dioxide (ZrO<sub>2</sub>) in a fast exothermic reaction.<sup>58</sup>

A 2008 Journal of Nuclear Materials paper, “Zircaloy-4 and M5 High Temperature Oxidation and Nitriding in Air,” explains that “once initiated, the nitride-assisted degradation will be a self-sustaining process, because ZrN conversion into oxide leaves nitrogen trapped in the oxide scale and available for further nitriding, and because the oxide formed is undoubtedly non-protective. Where nitriding has initiated, the bright  $\alpha$ -Zr(O) layer is thin, confirming the faster progression of the oxidation front there. The

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<sup>53</sup> J. Stuckert, M. Große, Z. Hózer, M. Steinbrück, Karlsruhe Institute of Technology, “Results of the QUENCH-16 Bundle Experiment on Air Ingress,” KIT-SR 7634, May 2013, p. 1; and O. Coindreau, C. Duriez, S. Ederli, “Air Oxidation of Zircaloy-4 in the 600-1000°C Temperature Range: Modeling for ASTEC Code Application,” Journal of Nuclear Materials 405, 2010, p. 208.

<sup>54</sup> J. Stuckert *et al.*, “Results of the QUENCH-16 Bundle Experiment on Air Ingress,” p. 1.

<sup>55</sup> Dana A. Powers, Chairman of ACRS, Letter to Richard A. Meserve, Chairman of NRC, Regarding ACRS Recommendations for Improvements to the NRC Staff’s “Technical Study of Spent Fuel Pool Accident Risk at Decommissioning Nuclear Power Plants,” April 13, 2000, (ADAMS Accession No. ML003704532), p. 2.

<sup>56</sup> O. Coindreau, C. Duriez, S. Ederli, “Air Oxidation of Zircaloy-4 in the 600-1000°C Temperature Range: Modeling for ASTEC Code Application,” p. 207.

<sup>57</sup> J. Stuckert *et al.*, “Results of the QUENCH-16 Bundle Experiment on Air Ingress,” p. 10.

<sup>58</sup> Emilie Beuzet *et al.*, “Modelling of Zry-4 Cladding Oxidation by Air Under Severe Accident Conditions using MAAP4 Code,” International Conference Nuclear Energy for New Europe 2009, Slovenia, September 2009, p. 3.

self-sustainability of the nitriding-reoxidation sequence may also favor the lateral progressive propagation of the breakaway.”<sup>59</sup>

Regarding nitrogen-induced breakaway oxidation, the 2008 Journal of Nuclear Materials paper explains that “[b]reakdown and loss of the dense scale protective effect occur and result in an accelerated degradation;” furthermore, the transition to nitrogen-induced breakaway oxidation occurs *earlier with pre-oxidized fuel cladding* than with fresh *non-oxidized* fuel cladding—“nitriding is favored by the ‘corrosion’ scale.”<sup>60</sup>

It is clear that *in air*, in a SFP accident, a significant degree of zirconium oxidation would occur, because spent fuel rods would be “pre-oxidized.” When high burnup (and other) fuel rods are discharged from the reactor core and loaded into the SFP, the fuel cladding can have local zirconium dioxide (ZrO<sub>2</sub>) “oxide” layers that are up to 100 µm thick (or greater); there can also be local crud layers on top of the oxide layers, which can sometimes also be up to 100 µm thick. And medium to high burnup fuel cladding typically has a “hydrogen concentration in the range of 100-1000 wppm [weight parts per million];” “[z]irconium-based alloys, in general, have a strong affinity for oxygen, nitrogen, and hydrogen...”<sup>61</sup>

Regarding the fact that air oxidation causes a fast progression of the oxidation front, the 2008 Journal of Nuclear Materials paper states:

At 800°C and above, continuous acceleration is observed, as the consequence of a complex process involving nitride formation and re-oxidation, as well as dissolution of nitrogen in the zirconia anion sublattice. Important volume mismatches of the ZrO<sub>2</sub> and ZrN compounds, together with zirconia phase transformations lead to *growth of a highly cracked, porous, non-protective oxide. It results in fast progression of the oxidation front, as well as strong deformation of the cladding.* The barrier against fission product release provided by the fuel cladding is lost much earlier than during accident under steam atmosphere<sup>62</sup> [emphasis added].

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<sup>59</sup> C. Duriez, T. Dupont, B. Schmet, F. Enoch, “Zircaloy-4 and M5 High Temperature Oxidation and Nitriding in Air,” Journal of Nuclear Materials 380 (2008), p. 43.

<sup>60</sup> *Id.*, p. 44.

<sup>61</sup> K. Natesan, W.K. Soppet, Argonne National Laboratory, “Hydrogen Effects on Air Oxidation of Zirlo Alloy,” NUREG/CR-6851, October 2004, (ADAMS Accession No: ML042870061), p. iii, 3.

<sup>62</sup> C. Duriez, T. Dupont, B. Schmet, F. Enoch, “Zircaloy-4 and M5 High Temperature Oxidation and Nitriding in Air,” Journal of Nuclear Materials 380 (2008), p. 44.

And regarding the fact that cladding degradation can be even much faster in oxygen starved situations (in air), the 2008 Journal of Nuclear Materials paper states:

Kinetic data of this study have been obtained mainly in high air flow conditions. *In real accidental situations, where oxygen starved situations are likely to occur, cladding degradation can be even much faster than predictable from these high air flow data*, because of early initiation of the nitriding process, as shown by the few tests performed at the highest temperatures with insufficient air flow rate. All in all, more experimental investigations are required to address the various conditions that can be encountered in accidental situation.<sup>63</sup>

### **III.A.6. The Axial and Radial Propagation of a Spent Fuel Pool Fire**

Regarding the axial propagation of the zirconium-*steam* reaction from its point of initiation, a 1990 Karlsruhe report, KfK 4378, states:

[T]he temperature escalation starts at the hottest position in the bundle [of fuel rod simulators], at an elevation above the middle. From there, slowly moving fronts of bright light, which illuminated the bundle, were seen, indicating the spreading of the temperature escalation upward and downward.<sup>64</sup>

And regarding axial and radial propagation of the zirconium-oxygen reaction (in steam and/or air), a September 2013 NRC document, NUREG-2157, states:

Under certain conditions, the high temperature runaway zirconium oxidation reaction occurring in one part of the pool could also spread to other spent fuel in the pool. The proximity of fuel assemblies to one another, combined with the effects of [radiative] heat transfer when these assemblies are at very high temperatures, could allow the runaway oxidation reaction to spread from spent fuel with high decay heat to spent fuel with lower decay heat that would otherwise not have begun burning.<sup>65</sup>

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<sup>63</sup> *Id.*

<sup>64</sup> S. Hagen, P. Hofmann, G. Schanz, L. Sepold, “Interactions in Zircaloy/VO<sub>2</sub> Fuel Rod Bundles with Inconel Spacers at Temperatures above 1200°C (Posttest Results of Severe Fuel Damage Experiments CORA-2 and CORA-3),” Forschungszentrum Karlsruhe, KfK 4378, September 1990, p. 41.

<sup>65</sup> NRC, “Waste Confidence Generic Environmental Impact Statement: Draft Report for Comment,” NUREG-2157, Appendix F, p. F-2.

As fuel rods heated up to melting temperatures, “the steel racks supporting the fuel assemblies will also heat due to convection and radiation from the fuel assemblies.”<sup>66</sup> In the worst-case scenario, a SFP fire would propagate “throughout the entire spent fuel inventory in the pool”<sup>67</sup>

The zirconium-air reaction would propagate away from its point of initiation more rapidly than the propagation of the zirconium-steam reaction, because: 1) the heat produced by zirconium oxidation in air is greater than that in steam; 2) the nitrogen content in air would accelerate zirconium oxidation in air; and 3) heat would also be contributed by the exothermic zirconium-nitrogen reaction.

### **III.B. Deficiencies of the NRC MELCOR Computer Safety Model, Regarding the Zirconium-Oxygen and Zirconium-Nitrogen Reactions in Air**

#### **III.B.1. MELCOR Does Not Model the Exothermic Zirconium-Nitrogen Reaction**

NRC has recently performed a number of post-Fukushima computer simulations of SFP accidents with the Sandia National Laboratories (“SNL”) MELCOR computer safety model. However, MELCOR *does not simulate* the generation of heat from the chemical reaction of zirconium and nitrogen; neglecting to model a heat source that would affect the progression and severity of SFP accidents is a serious flaw.

Regarding limitations of NRC’s MELCOR computer safety model, in 2006, a SNL report observed that MELCOR *does not* model the nitriding of zirconium fuel cladding, stating that fuel cladding would “combine with nitrogen if no oxygen or steam are available” and that the nitriding process is exothermic (heat-generating).<sup>68</sup> And in August 2012 a different SNL report, “Fukushima Daiichi Accident Study” stated: “If *inadequate* cooling is provided, then the cladding will heat up and will rapidly oxidize (*i.e.*, burn) and to a lesser extent, nitride (*i.e.*, combine with nitrogen if no oxygen or

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<sup>66</sup> K. C. Wagner, R. O. Gauntt, Sandia National Laboratories, Analysis and Modeling Division, “Mitigation of Spent Fuel Pool Loss-of-Coolant Inventory Accidents and Extension of Reference Plant Analyses to Other Spent Fuel Pools,” SAND1A Letter Report, Revision 2, p. 12.

<sup>67</sup> J.H. Jo, P.F. Rose, S.D. Unwin, V.L. Sailor, Brookhaven National Laboratory, “Value/Impact Analyses of Accident Preventive and Mitigative Options for Spent Fuel Pools,” NUREG/CR-5281, March 1989, (ADAMS Accession No. ML071690022), p. 8.

<sup>68</sup> K. C. Wagner, R. O. Gauntt, Sandia National Laboratories, Analysis and Modeling Division, “Mitigation of Spent Fuel Pool Loss-of-Coolant Inventory Accidents and Extension of Reference Plant Analyses to Other Spent Fuel Pools,” SAND1A Letter Report, Revision 2, p. 12.

steam are available). *Since the oxidation and nitride processes are exothermic*, the fuel rods could heat to melting conditions and structurally degrade”<sup>69</sup> [emphasis added].

In an *April 2000* letter from Dana A. Powers, Chairman of ACRS, to Richard A. Meserve, Chairman of NRC, ACRS advised the NRC Staff that an NRC report on SFP accident risk “relied on relatively geriatric work” for its *analysis of the interaction of air with zirconium fuel cladding*, stating that “[m]uch more is known now about air interactions with cladding,” including knowledge gained “from studies being performed as part of a cooperative international program (PHEBUS FP<sup>70</sup>) in which NRC is a partner.” ACRS told the NRC Staff that “[a]mong the findings of this work *is that nitrogen from air depleted of oxygen will interact exothermically with zircaloy cladding*. The reaction of zirconium with nitrogen is exothermic by about 86,000 calories per mole of zirconium reacted. Because the heat required to raise zirconium from room temperature to melting is only about 18,000 calories per mole, the reaction enthalpy with nitrogen is ample”<sup>71</sup> [emphasis added].

As early as 1987, a report that was prepared for NRC, “Severe Accidents in Spent Fuel Pools in Support of Generic Safety Issue 82,” stated that zirconium nitriding in air is an exothermic reaction, “releasing approximately 82 kcal/mole”—approximately 3.76 megajoules per kg of Zr reacted,<sup>72</sup> which is approximately 30 percent of the quantity of energy (per kg of Zr reacted) produced by the zirconium-oxygen reaction in air. Unfortunately, more than 25 years later, NRC’s Post-Fukushima MELCOR simulations still do not model how the nitrogen content of air would affect the progression of a SFP accident.

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<sup>69</sup> Randall Gauntt *et al.*, Sandia National Laboratories, “Fukushima Daiichi Accident Study: Status as of April 2012,” SAND2012-6173, August 2012, p. 183.

<sup>70</sup> PHEBUS FP is an experimental program that researched severe-accident reactor core damage.

<sup>71</sup> Dana A. Powers, Chairman of ACRS, Letter to Richard A. Meserve, Chairman of NRC, Regarding ACRS Recommendations for Improvements to the NRC Staff’s “Technical Study of Spent Fuel Pool Accident Risk at Decommissioning Nuclear Power Plants,” April 13, 2000, (ADAMS Accession No. ML003704532), pp. 3-4.

<sup>72</sup> V. L. Sailor *et al.*, Brookhaven National Laboratory, “Severe Accidents in Spent Fuel Pools in Support of Generic Safety Issue 82,” NUREG/CR-4982, July 1987, p. 109.

### III.B.2. MELCOR Does Not Model How Nitrogen Accelerates the Oxidation and Degradation of Zirconium Fuel-Cladding in Air

MELCOR also *does not simulate* how nitrogen gas (in air) affects the oxidation of zirconium in air.<sup>73</sup> This is a serious flaw because the presence of nitrogen accelerates the oxidation (burning) and degradation of zirconium fuel-cladding *in air*,<sup>74</sup> which would affect the progression and severity of a SFP accident, including radioactive releases, “most notabl[y] ruthenium.”<sup>75</sup> (“Ruthenium has a biological effectiveness equivalent to that of Iodine-131;”<sup>76</sup> Ruthenium-106 has half-life of 373.6 days.) Hence, NRC’s MELCOR simulations of SFP accidents *under-predict* the severity of such accidents.

A 2010 Journal of Nuclear Materials paper observes that “[t]he complexity of air oxidation of Zircaloy arises out of the simultaneous oxidation and nitriding processes.”<sup>77</sup> And a May 2013 report, “Results of the QUENCH-16 Bundle Experiment on Air Ingress,” discusses experimental data demonstrating that porous nitrides form inside oxide layers *under local or full oxygen-starvation conditions*.<sup>78</sup> (When zirconium reacts in air it is possible for the reaction to become oxygen-starved; however, if zirconium is locally oxygen-starved in air, nitrogen will react with it.) The porous, degraded condition of an oxide layer facilitates accelerated oxidation rates if additional oxygen becomes *locally* available; and any additional oxygen will react with the zirconium nitride (ZrN)

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<sup>73</sup> K. C. Wagner, R. O. Gauntt, Sandia National Laboratories, Analysis and Modeling Division, “Mitigation of Spent Fuel Pool Loss-of-Coolant Inventory Accidents and Extension of Reference Plant Analyses to Other Spent Fuel Pools,” SAND1A Letter Report, Revision 2, p. 12; and L. Fernandez-Moguel, J. Birchley, European MELCOR User’s Group, “PSI air oxidation model in MELCOR: Part 2: Analysis of experiments and model assessment,” Stockholm, May 2013, which states: “Neither MELCOR nor SCDAP [a severe accident computer safety model] are able to predict a nitride reaction.”

<sup>74</sup> J. Stuckert, M. Große, Z. Hózer, M. Steinbrück, Karlsruhe Institute of Technology, “Results of the QUENCH-16 Bundle Experiment on Air Ingress,” KIT-SR 7634, May 2013, p. 1; and O. Coindreau, C. Duriez, S. Ederli, “Air Oxidation of Zircaloy-4 in the 600-1000°C Temperature Range: Modeling for ASTEC Code Application,” p. 208.

<sup>75</sup> J. Stuckert *et al.*, “Results of the QUENCH-16 Bundle Experiment on Air Ingress,” p. 1.

<sup>76</sup> Dana A. Powers, Chairman of ACRS, Letter to Richard A. Meserve, Chairman of NRC, Regarding ACRS Recommendations for Improvements to the NRC Staff’s “Technical Study of Spent Fuel Pool Accident Risk at Decommissioning Nuclear Power Plants,” p. 2.

<sup>77</sup> O. Coindreau, C. Duriez, S. Ederli, “Air Oxidation of Zircaloy-4 in the 600-1000°C Temperature Range: Modeling for ASTEC Code Application,” p. 207.

<sup>78</sup> J. Stuckert *et al.*, “Results of the QUENCH-16 Bundle Experiment on Air Ingress,” p. 10.



within an existing oxide layer and form zirconium dioxide ( $\text{ZrO}_2$ ) in a fast exothermic reaction.<sup>79</sup>

As quoted above, an *April 2000* ACRS letter states that “[m]uch more is known now about air interactions with cladding;”<sup>80</sup> however, a 2008 Journal of Nuclear Materials paper, “Zircaloy-4 and M5 High Temperature Oxidation and Nitriding in Air,” states:

Oxidation of zirconium alloys at high temperature for severe accident analysis has been widely studied in steam, however, the existing data regarding air oxidation in the temperature range of interest are scarce. ...the exact role of zirconium nitride on the cladding degradation process is poorly understood. It remains unclear to [what] extent the nitrogen effect is responsible for the kinetic acceleration of the oxidation process that has been observed by these authors.

Further[more], it should be stressed that most of the existing data have been obtained with bare [non-oxidized] samples.<sup>81</sup>

Regarding nitrogen-induced breakaway oxidation, the 2008 Journal of Nuclear Materials paper explains that “[b]reakdown and loss of the dense scale protective effect occur and result in an accelerated degradation;” furthermore, the transition to nitrogen-induced breakaway oxidation occurs *earlier with pre-oxidized fuel cladding* than with fresh *non-oxidized* fuel cladding—“nitriding is favored by the ‘corrosion’ scale.”<sup>82</sup>

It is clear that *in air*, in a SFP accident, a significant degree of zirconium oxidation would occur, because spent fuel rods would be “pre-oxidized.” When high burnup (and other) fuel rods are discharged from the reactor core and loaded into the SFP, the fuel cladding can have local zirconium dioxide ( $\text{ZrO}_2$ ) “oxide” layers that are up to 100  $\mu\text{m}$  thick (or greater); there can also be local crud layers on top of the oxide layers, which can sometimes also be up to 100  $\mu\text{m}$  thick. And medium to high burnup fuel cladding typically has a “hydrogen concentration in the range of 100-1000 wppm [weight

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<sup>79</sup> Emilie Beuzet *et al.*, “Modelling of Zry-4 Cladding Oxidation by Air Under Severe Accident Conditions using MAAP4 Code,” International Conference Nuclear Energy for New Europe 2009, Slovenia, September 2009, p. 3.

<sup>80</sup> Dana A. Powers, Chairman of ACRS, Letter to Richard A. Meserve, Chairman of NRC, Regarding ACRS Recommendations for Improvements to the NRC Staff’s “Technical Study of Spent Fuel Pool Accident Risk at Decommissioning Nuclear Power Plants,” p. 3.

<sup>81</sup> C. Duriez, T. Dupont, B. Schmet, F. Enoch, “Zircaloy-4 and M5 High Temperature Oxidation and Nitriding in Air,” Journal of Nuclear Materials 380 (2008), p. 30.

<sup>82</sup> *Id.*, p. 44.

parts per million];” “[z]irconium-based alloys, in general, have a strong affinity for oxygen, nitrogen, and hydrogen...”<sup>83</sup>

Regarding limitations of air oxidation models, the May 2013 report, “Results of the QUENCH-16 Bundle Experiment on Air Ingress,” states that “[t]he models for air oxidation do not yet cover the whole range of representative conditions. The main aims of new bundle tests should be the investigation of areas where data [are] mostly missing.”<sup>84</sup> And, a 2009 paper, regarding needed development for MELCOR *in the area of air ingress*, states that “air oxidation cannot be reliably predicted (or even described conservatively) by any of the models used in the currently available codes. A new modeling approach and an appropriate database are therefore necessary.”<sup>85</sup> Additionally, information about the French Mozart Program to study the zirconium-air reaction states that “[b]ibliographic reviews reveal wide scattering of the existing kinetic data concerning the oxidation of Zircaloy-4 by air in the temperature range concerned [600°C to 1200°C]. *For recent alloys, such as M5 and Zirlo, there is virtually no data published in the open literature*”<sup>86</sup> [emphasis added].

In a June 2013 document, NRC explained that a new air oxidation kinetics model was added to MELCOR version 1.8.6 (2005) that is based on data from *isothermal*<sup>87</sup> air zirconium-oxidation experiments conducted at Argonne National Laboratory (“ANL”). The ANL data (published in 2004) demonstrated that “air oxidation can be observed at temperatures as low as 600 K [327°C (620°F)];” and that the breakaway phenomenon that occurs when zirconium is oxidized in air causes “a sharp increase” in reaction and

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<sup>83</sup> K. Natesan, W.K. Soppet, Argonne National Laboratory, “Hydrogen Effects on Air Oxidation of Zirlo Alloy,” NUREG/CR-6851, October 2004, (ADAMS Accession No. ML042870061), p. iii, 3.

<sup>84</sup> J. Stuckert *et al.*, “Results of the QUENCH-16 Bundle Experiment on Air Ingress,” p. 1.

<sup>85</sup> S. Güntay, J. Birchley, “MELCOR Further Development in the Area of Air Ingress and Participation in OECDNEA SFP Project to Be Performed in the Time Frame 2009-2012,” April 2009, p. 4.

<sup>86</sup> IRSN, website description of the Mozart Program; available at: <http://www.irsn.fr/EN/Research/Research-organisation/Research-programmes/SOURCE-TERM/MOZART/Pages/The-MOZART-programme-on-the-PWR-fuel-cladding-oxidation-in-air-3238.aspx> (last visited 10/22/13).

<sup>87</sup> The tests ANL were *isothermal tests*, in which “a [zirconium alloy] specimen was held at constant temperature and the weight gain associated with oxidation as a function of time was measured.” See NRC, “Consequence Study of a Beyond-Design-Basis Earthquake Affecting the Spent Fuel Pool for a U.S. Mark I Boiling Water Reactor: Draft Report,” p. 93.

heatup rates in the post-breakaway regime. Apparently, MELCOR version 1.8.6 “provide[s] a better prediction of the measured data, including a transition to accelerated post-breakaway oxidation kinetics.”<sup>88</sup>

MELCOR version 1.8.6 may provide a “better prediction” of the measured air oxidation data, than older versions. However, the Paul Scherrer Institute (“PSI”) recently assessed MELCOR 1.8.6’s ability to predict fuel-cladding behavior in accidents involving air ingress into the reactor vessel—which is pertinent to MELCOR’s ability to predict zirconium-air reaction rates in SFP accidents—and “concluded that development of MELCOR was needed *to capture the accelerated cladding oxidation that can take place under air ingress conditions* (characterized by transition from formation of a protective oxide film to non-protective ‘breakaway’ oxidation at a significantly higher rate)”<sup>89</sup> [emphasis added].

PSI has also explained:

Although there was not, [in] the 1980’s, any systematic treatment of air oxidation, correlations had been developed on the basis of limited data<sup>90</sup> and these had been adapted for use in MELCOR in [an] attempt to provide a conservative statement of the thermal response to an air ingress scenario. A feature of all these correlations was that the controlling processes were similar to those which govern steam oxidation. The US-NRC later commissioned experimental studies<sup>91</sup> [the ANL isothermal experiments] to obtain data with which to establish a credible physical basis for using the correlations. *More recent experiments*<sup>92</sup> *demonstrated that the*

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<sup>88</sup> NRC, “Consequence Study of a Beyond-Design-Basis Earthquake Affecting the Spent Fuel Pool for a U.S. Mark I Boiling Water Reactor: Draft Report,” pp. 93-94.

<sup>89</sup> S. Güntay, J. Birchley, “MELCOR Further Development in the Area of Air Ingress and Participation in OECDNEA SFP Project to Be Performed in the Time Frame 2009-2012,” April 2009, p. 2.

<sup>90</sup> A. Benjamin *et al.*, “Spent Fuel Heatup following Loss of Water during Storage,” NUREG/CR-0649, SAND77-1371, March 1979, (ADAMS Accession No. ML120960637); and V. Sailor *et al.*, “Severe Accidents in Spent Fuel Ponds in Support of Generic Issue 82,” NUREG/CR-4982, July 1987.

<sup>91</sup> K. Natesan, W.K. Soppet, Argonne National Lab (ANL), “Air Oxidation Kinetics for Zr-Based Alloys,” NUREG/CR-6846, July 2004, (ADAMS Accession No. ML041900069).

<sup>92</sup> These recent experiments are discussed in the four following reports: 1) M. Steinbrueck, U. Stegmeier, T. Ziegler, “Prototypical Experiments on Air Oxidation of Zircaloy-4 at High Temperature,” FZK 7257, January 2007; 2) G. Schanz *et al.*, “Results of QUENCH-10 Experiment on Air Ingress,” FZKA 7057, May 2006; 3) Ch. Duriez *et al.*, “Separate effect Tests on Zirconium Cladding Degradation in Air Ingress Situations,” Proceedings of 2nd ERMSAR Conference, Karlsruhe, Germany, 2007; and 4) A. Auvinen *et al.*, “Progress on ruthenium release and transport under air ingress Conditions,” Nuclear Engineering and Design, 238, 2008, pp. 3418–3428.

*processes that govern air oxidation are quite different from those which apply to steam oxidation*<sup>93</sup> [emphasis added].

Clearly, NRC's conclusions from its Post-Fukushima MELCOR simulations are non-conservative *and misleading*, because their conclusions *underestimate* the probabilities of large radiological releases from SFP accidents. By overlooking the deficiencies of its Post-Fukushima MELCOR simulations, the NRC undermines its own philosophy of defense-in-depth, which requires the application of conservative models.<sup>94</sup>

### **III.B.3. NRC's Recent Non-Conservative Post-Fukushima MELCOR Simulations**

A recent NRC Post-Fukushima MELCOR (version 1.8.6 of the code<sup>95</sup>) simulation of *a particular* BWR Mark I SFP fire scenario ("Unsuccessful Deployment of Mitigation for Moderate Leak (OCP3) Scenario"<sup>96</sup>) found that in the central area of the SFP, "Radial Ring 1"—where the newly discharged, hottest, fuel assemblies were stored—the peak fuel-cladding temperature would reach approximately 1800 K (1527°C) (2780°F) at "Axial Level 4."<sup>97</sup> However, the same simulation also found that "[a]fter the peak temperature [is reached] at [Axial] Level 4, the peak temperature in the zirconium fire front decreases with each successive [axial] level. Radial heat transfer<sup>98</sup> from the fuel racks to the SFP wall..., *the buildup of the oxide layer on the fuel, and the depletion of*

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<sup>93</sup> S. Guntay, J. Birchley, "MELCOR Further Development in the Area of Air Ingress and Participation in OECDNEA SFP Project to Be Performed in the Time Frame 2009-2012," p. 4.

<sup>94</sup> Charles Miller *et al.*, NRC, "Recommendations for Enhancing Reactor Safety in the 21st Century: The Near-Term Task Force Review of Insights from the Fukushima Dai-ichi Accident," SECY-11-0093, July 12, 2011, (ADAMS Accession No. ML111861807), p. 3.

<sup>95</sup> The SFP models in MELCOR versions 1.8.6 and 2.1 are functionally the same. See NRC, "Consequence Study of a Beyond-Design-Basis Earthquake Affecting the Spent Fuel Pool for a U.S. Mark I Boiling Water Reactor: Draft Report," pp. 92-93.

<sup>96</sup> NRC, "Consequence Study of a Beyond-Design-Basis Earthquake Affecting the Spent Fuel Pool for a U.S. Mark I Boiling Water Reactor: Draft Report," p. 142.

<sup>97</sup> For MELCOR "[t]he core is nodalized into a number of axial levels and radial rings (each ring represents a collection of assemblies);" and "MELCOR core models were originally designed for the reactor core. Because of the code flexibility, the same modeling approach can be used for the spent fuel pool (with the addition of the rack as a separate component)." See NRC, "Consequence Study of a Beyond-Design-Basis Earthquake Affecting the Spent Fuel Pool for a U.S. Mark I Boiling Water Reactor: Draft Report," p. 95, and p. 95, Note 12.

<sup>98</sup> "MELCOR attempts to model a multidimensional geometry with a simplified two-surface radiation model." See NRC, "Consequence Study of a Beyond-Design-Basis Earthquake Affecting the Spent Fuel Pool for a U.S. Mark I Boiling Water Reactor: Draft Report," p. 110, Note 23.

*the oxygen in the reactor building...cause the clad temperature to decrease. After 24 hours, the fuel temperatures in [Radial] Ring 1 are relatively stable*”<sup>99</sup> [emphasis added]. (In this scenario there is a depletion of the oxygen in the reactor building, because the reactor building was *not* breached by a hydrogen explosion (a total of four reactor buildings were breached by hydrogen explosions in the Fukushima Dai-ichi accident<sup>100</sup>).

This recent NRC MELCOR simulation—in which there is a depletion of the oxygen in the reactor building—would have had *different results* if it had modeled: 1) how nitriding would degrade the fuel-cladding’s “protective” oxide layer and accelerate the zirconium oxidation, which would contribute additional heat; 2) the nitriding of zirconium under oxygen-starvation conditions; and 3) the significant additional heat that would be contributed from the exothermic nitrogen-zirconium reaction.

In other recent NRC MELCOR simulations of BWR Mark I SFP accident/fire scenarios, the reactor buildings were breached by hydrogen explosions, so there was more available oxygen to facilitate zirconium oxidation. However, those simulations would have had *different results* if they had modeled: 1) how nitriding would degrade the fuel-cladding’s “protective” oxide layer and accelerate the zirconium oxidation, which would contribute additional heat and 2) the significant additional heat that would be contributed from the exothermic nitrogen-zirconium reaction.<sup>101</sup>

In actual SFP fires, there would be quicker fuel-cladding temperature escalations, releasing more heat, and quicker axial and radial propagation of zirconium fires than MELCOR indicates.

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<sup>99</sup> NRC, “Consequence Study of a Beyond-Design-Basis Earthquake Affecting the Spent Fuel Pool for a U.S. Mark I Boiling Water Reactor: Draft Report,” pp. 142-143.

<sup>100</sup> In the Fukushima Dai-ichi accident, hydrogen detonated in and essentially destroyed the secondary containments of Units 1, 3, and 4, causing large releases of radiation. And the secondary containment of Unit 2 was breached: a hydrogen explosion that occurred in the Unit 1 reactor building “caused a blowout panel in the Unit 2 reactor building to open, which resulted in a loss of secondary containment integrity.” See INPO, “Special Report on the Nuclear Accident at the Fukushima Dai-ichi Nuclear Power Station,” INPO 11-005, November 2011, p. 24.

<sup>101</sup> NRC, “Consequence Study of a Beyond-Design-Basis Earthquake Affecting the Spent Fuel Pool for a U.S. Mark I Boiling Water Reactor: Draft Report.”

### **III.B.4. Recent Sandia National Laboratory Spent Fuel Pool Accident Experiments Are Unrealistic because They Were Conducted with Clean Non-Oxidized Cladding**

Recent Sandia National Laboratory (“SNL”) SFP accident experiments are unrealistic because they have been conducted with clean non-oxidized bundles of zirconium fuel rod simulators;<sup>102</sup> the spent fuel assemblies stored in SFPs have oxide layers. When high burnup (and other) fuel rods are discharged from the reactor core and loaded into the SFP, the fuel cladding can have local zirconium dioxide ( $\text{ZrO}_2$ ) “oxide” layers that are up to 100  $\mu\text{m}$  thick (or greater); there can also be local crud layers on top of the oxide layers, which can sometimes also be up to 100  $\mu\text{m}$  thick. And medium to high burnup fuel cladding typically has a “hydrogen concentration in the range of 100-1000 wppm [weight parts per million];” “[z]irconium-based alloys, in general, have a strong affinity for oxygen, nitrogen, and hydrogen...”<sup>103</sup>

Regarding nitrogen-induced breakaway oxidation, the 2008 Journal of Nuclear Materials paper explains that “[b]reakdown and loss of the dense scale protective effect occur and result in an accelerated degradation;” furthermore, the transition to nitrogen-induced breakaway oxidation occurs *earlier with pre-oxidized fuel cladding* than with fresh *non-oxidized* fuel cladding—“nitriding is favored by the ‘corrosion’ scale.”<sup>104</sup>

It is clear that *in air*, in a SFP accident, there would be a significant degree of zirconium oxidation, because the spent fuel rods in the pool would be “pre-oxidized.” This phenomenon of nitrogen attacking pre-oxidized zirconium cladding is not simulated in SNL’s experiments. Hence, data from SNL’s SFP accident experiments is inadequate for benchmarking MELCOR. Benchmarking a computer safety model with data gathered

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<sup>102</sup> E. R. Lindgren, Sandia National Laboratory, “Characterization of Thermal-Hydraulic and Ignition Phenomena in Prototypic, Full-Length Boiling Water Reactor Spent Fuel Pool Assemblies After a Postulated Complete Loss-of-Coolant Accident,” NUREG/CR-7143, March 2013, (ADAMS Accession No. ML13072A056).

<sup>103</sup> K. Natesan, W.K. Soppet, Argonne National Laboratory, “Hydrogen Effects on Air Oxidation of Zirlo Alloy,” NUREG/CR-6851, October 2004, (ADAMS Accession No: ML042870061), p. iii, 3.

<sup>104</sup> C. Duriez, T. Dupont, B. Schmet, F. Enoch, “Zircaloy-4 and M5 High Temperature Oxidation and Nitriding in Air,” Journal of Nuclear Materials 380 (2008), p. 44.

from unrealistic experiments undermines the NRC's philosophy of defense-in-depth, which requires the application of conservative models.<sup>105</sup>

### **III.C. Experimental Data Indicates that MELCOR Under-Predicts the Zirconium-Steam Reaction Rates that Would Occur in a Spent Fuel Pool Accident**

#### **III.C.1. Oxidation Models Are Not Able to Predict the Fuel-Cladding Temperature Escalation that Commenced at “Low Temperatures” in the PHEBUS B9R-2 Test**

As stated above, the PHEBUS B9R test was conducted in a light water reactor—as part of the PHEBUS severe fuel damage program—with an assembly of 21 UO<sub>2</sub> fuel rods. The B9R test was conducted in two parts: the B9R-1 test and the B9R-2 test.<sup>106</sup> A 1996 European Commission report states that the B9R-2 test had an unexpected fuel-cladding temperature escalation in the mid-bundle region; the highest temperature escalation rates were from 20°C/sec (36°F/sec) to 30°C/sec (54°F/sec).<sup>107</sup>

Discussing PHEBUS B9R-2, the 1996 European Commission report states:

The B9R-2 test (second part of B9R) illustrates the oxidation in different cladding conditions representative of a pre-oxidized and fractured state. This state results from a first oxidation phase (first part name B9R-1, of the B9R test) terminated by a rapid cooling-down phase. During B9R-2, an unexpected strong escalation of the oxidation of the remaining Zr occurred when the bundle flow injection was switched from helium to steam while the maximum clad temperature was equal to 1300 K [1027°C (1880°F)]. *The current oxidation model was not able to predict the strong heat-up rate observed* even taking into account the measured large clad deformation and the double-sided oxidation (final state of the cladding from macro-photographs).

*... No mechanistic model is currently available to account for enhanced oxidation of pre-oxidized and cracked cladding*<sup>108</sup> [emphasis added].

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<sup>105</sup> Charles Miller *et al.*, NRC, “Recommendations for Enhancing Reactor Safety in the 21st Century: The Near-Term Task Force Review of Insights from the Fukushima Dai-ichi Accident,” SECY-11-0093, p. 3.

<sup>106</sup> G. Hache, R. Gonzalez, B. Adroguer, Institute for Protection and Nuclear Safety, “Status of ICARE Code Development and Assessment,” in NRC “Proceedings of the Twentieth Water Reactor Safety Information Meeting,” NUREG/CP-0126, Vol. 2, 1992, (ADAMS Accession No: ML042230126), p. 311.

<sup>107</sup> T.J. Haste *et al.*, “In-Vessel Core Degradation in LWR Severe Accidents,” European Commission, Report EUR 16695 EN, 1996, p. 33.

<sup>108</sup> *Id.*, p. 126.

Today, in 2013, oxidation models still cannot accurately predict the local fuel-cladding temperature escalation that commenced in PHEBUS B9R-2 *in steam* when local fuel-cladding temperatures were 1027°C (1880°F). The PHEBUS B9R-2 results indicate that the currently used zirconium-steam reaction correlations, such as the Cathcart-Pawel and Urbanic-Heidrick correlations, are inadequate for use in computer safety models like MELCOR.

### **III.C.2. “Low Temperature” Oxidation Rates Are Under-Predicted for the CORA-16 Experiment**

When Oak Ridge National Laboratory (“ORNL”) investigators compared the results of the CORA-16 experiment—a BWR core severe fuel damage test, simulating a meltdown, conducted with a multi-rod zirconium alloy bundle—with the predictions of computer safety models, they found that the zirconium-steam reaction rates that occurred in the experiment were under-predicted. The investigators concluded that the “application of the available Zircaloy oxidation kinetics models [zirconium-steam reaction correlations] causes the low-temperature [1652-2192°F] oxidation to be underpredicted.”<sup>109</sup>

It has been postulated that cladding strain—ballooning—was a factor in increasing the zirconium-steam reaction rates that occurred in CORA-16.<sup>110</sup> However, it is *unsubstantiated* that cladding strain actually increased reaction rates.

To help explain how cladding strain could have been a factor in increasing the zirconium-steam reaction rates that occurred in CORA-16, the NRC has pointed out that an NRC report, NUREG/CR-4412,<sup>111</sup> “explain[s] that under *certain* conditions

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<sup>109</sup> L. J. Ott, Oak Ridge National Laboratory, “Report of Foreign Travel of L. J. Ott, Engineering Analysis Section, Engineering Technology Division,” ORNL/FTR-3780, October 16, 1990, p. 3.

<sup>110</sup> L. J. Ott, W. I. van Rij, “In-Vessel Phenomena—CORA: BWR Core Melt Progression Phenomena Program, Oak Ridge National Laboratory,” CONF-9105173-3-Extd.Abst., Presented at Cooperative Severe Accident Research Program, Semiannual Review Meeting, Bethesda, Maryland, May 6-10, 1991.

<sup>111</sup> R. E. Williford, “An Assessment of Safety Margins in Zircaloy Oxidation and Embrittlement Criteria for ECCS Acceptance,” NUREG/CR-4412, April 1986, (ADAMS Accession No: ML083400371).



ballooning and deformation of the cladding can increase the available surface area for oxidation, thus enhancing the apparent oxidation rate”<sup>112</sup> [emphasis not added].

Regarding this phenomenon, NUREG/CR-4412 states:

Depressurization of the primary coolant during a LB LOCA or [severe accident] will permit [fuel] cladding deformation (ballooning and possibly rupture) to occur because the fuel rod internal pressure may be greater than the external (coolant) pressure. In this case, oxidation and deformation can occur simultaneously. This in turn may result in an apparent enhancement of oxidation rates because: 1) ballooning increases the surface area of the cladding and permits more oxide to form per unit volume of Zircaloy and 2) the deformation may crack the oxide and provide increased accessibility of the oxygen to the metal. However deformation generally occurs before oxidation rates become significant; *i.e.*, below [1832°F]. Consequently, the lesser importance of this phenomenon has resulted in a relatively sparse database.<sup>113</sup>

NUREG/CR-4412 states that there is a *relatively sparse database* on the phenomenon of cladding strain enhancing zirconium-steam reaction rates.<sup>114</sup> NUREG/CR-4412 also explains that “it is possible to make a very crude estimate of the expected average enhancement of oxidation kinetics by deformation,”<sup>115</sup> the report provides a graph of the “rather sparse”<sup>116</sup> data. The graph indicates that the general trend is for cladding strain enhancements of zirconium-steam reaction rates to *decrease as cladding temperatures increase*.<sup>117</sup>

NUREG/CR-4412 has a brief description of the rather sparse data; in one case, two investigators (Furuta and Kawasaki), who heated specimens up to temperatures between 1292°F and 1832°F, reported that “[v]ery small enhancements [of reaction rates] occurred at about [eight percent] strain at [1832°F].”<sup>118</sup>

In fact, NUREG/CR-4412 states that only one pair of investigators (Bradhurst and Heuer) conducted tests that encompassed the temperature range—1652°F to 2192°F—in

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<sup>112</sup> NRC, “Draft Interim Review of PRM-50-93/95 Issues Related to the CORA Tests,” August 23, 2011, (ADAMS Accession No: ML112211930), p. 3.

<sup>113</sup> R. E. Williford, “An Assessment of Safety Margins in Zircaloy Oxidation and Embrittlement Criteria for ECCS Acceptance,” p. 27.

<sup>114</sup> *Id.*, pp. 27, 30.

<sup>115</sup> *Id.*, p. 30.

<sup>116</sup> *Id.*

<sup>117</sup> *Id.*, p. 29.

<sup>118</sup> *Id.*, p. 30.

which zirconium-steam reaction rates were under-predicted for CORA-16. Bradhurst and Heuer reported that “[m]aximum enhancements occurred at slower strain rates. ... However, the overall weight gain or average oxide thickness in [the Zircaloy-2 specimens] was only minimally increased because of the localization effects of cracks in the oxide layer.”<sup>119</sup> A second report states that “Bradhurst and Heuer...found no direct influence [from cladding strain] on Zircaloy-2 oxidation outside of oxide cracks.”<sup>120</sup> (In CORA-16, in the temperature range from 1652°F to 2192°F, cladding strain would have occurred over a very brief period of time, because cladding temperatures were increasing rapidly.)

Clearly, it is unsubstantiated that the estimated cladding strain accurately accounts for why reaction rates for CORA-16 were under-predicted in the temperature range from 1652°F to 2192°F. First, there is a relatively sparse database on how cladding strain enhances reaction rates. Second, the little data that is available indicates that cladding strain *may* only *slightly* enhance reaction rates at cladding temperatures of 1832°F and greater.<sup>121</sup>

Furthermore, ORNL papers on the BWR CORA experiments do not report that any experiments were conducted in order to confirm if in fact cladding strain actually increased zirconium-steam reaction rates and accounted for why reaction rates were under-predicted in the 1652°F to 2192°F temperature range for CORA-16.

There is also one phenomenon NRC did not consider in its 2011 analysis of CORA-16: “[t]he swelling of the [fuel] cladding...alters [the] pellet-to-cladding gap in a manner that provides less efficient energy transport from the fuel to the cladding,”<sup>122</sup> which would cause the local cladding temperature heatup rate to decrease as the cladding ballooned, moving away from the internal heat source of the fuel. The CORA

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<sup>119</sup> *Id.*

<sup>120</sup> F. J. Erbacher, S. Leistikow, “A Review of Zircaloy Fuel Cladding Behavior in a Loss-of-Coolant Accident,” Kernforschungszentrum Karlsruhe, KfK 3973, September 1985, p. 6.

<sup>121</sup> R. E. Williford, “An Assessment of Safety Margins in Zircaloy Oxidation and Embrittlement Criteria for ECCS Acceptance,” p. 30.

<sup>122</sup> Winston & Strawn LLP, “Duke Energy Corporation, Catawba Nuclear Station Units 1 and 2,” Enclosure, Testimony of Robert C. Harvey and Bert M. Dunn on Behalf of Duke Energy Corporation, “MOX Fuel Lead Assembly Program, MOX Fuel Characteristics and Behavior, and Design Basis Accident (LOCA) Analysis,” July 1, 2004, ((ADAMS Accession No: ML041950059), p. 43.

experiments were internally electrically heated (with annular uranium dioxide pellets to replicate uranium dioxide fuel pellets), so in CORA-16, the ballooning of the cladding would have had a mitigating factor on the local cladding temperature heatup rate, which, in turn, would have had a mitigating factor on zirconium-steam reaction rates.

CORA-16 is an example of an experiment that had zirconium-steam reaction rates that were under-predicted in the “low temperature” range from 1652°F to 2192°F by computer safety models. The CORA-16 results indicate that the currently used zirconium-steam reaction correlations, such as the Cathcart-Pawel and Urbanic-Heidrick correlations, are inadequate for use in computer safety models like MELCOR.

#### **IV. THE RATIONAL FOR THE PROPOSED REGULATIONS**

Recent NRC Post-Fukushima MELCOR simulations of BWR Mark I SFP accident/fire scenarios<sup>123</sup> would have had *different results* if they had modeled: 1) how nitriding would degrade the fuel-cladding’s “protective” oxide layer and accelerate the zirconium oxidation, which would contribute additional heat and 2) the significant additional heat that would be contributed from the exothermic nitrogen-zirconium reaction. The conclusions from such MELCOR simulations are non-conservative *and misleading*, because their conclusions *underestimate* the probabilities of large radiological releases from SFP accidents.

In actual SFP fires, there would be quicker fuel-cladding temperature escalations, releasing more heat, and quicker axial and radial propagation of zirconium fires than MELCOR indicates. Hence, in accordance with NRC’s philosophy of defense-in-depth, which requires the application of conservative models,<sup>124</sup> it is necessary to improve the performance of MELCOR and any other computer safety models that are intended to accurately simulate SFP accident/fire scenarios. The regulations proposed in this rulemaking petition, regarding zirconium fuel cladding oxidation and nitriding, are

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<sup>123</sup> NRC, “Consequence Study of a Beyond-Design-Basis Earthquake Affecting the Spent Fuel Pool for a U.S. Mark I Boiling Water Reactor: Draft Report.”

<sup>124</sup> Charles Miller *et al.*, NRC, “Recommendations for Enhancing Reactor Safety in the 21st Century: The Near-Term Task Force Review of Insights from the Fukushima Dai-ichi Accident,” SECY-11-0093, July 12, 2011, (ADAMS Accession No. ML111861807), p. 3.

intended to improve the performance of computer safety models that simulate postulated SFP accident/fire scenarios.

## **V. CONCLUSION**

If implemented, the regulations proposed in this petition for rulemaking would help improve public and plant-worker safety.

Respectfully submitted,

/s/

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Dated: December 23, 2013