UNITED STATES
NUCLEAR REGULATORY COMMISSION
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June 27, 1979

MEMORANDUM FOR: Roger J. Mattson, Director
Lessons Learned Task Force

FROM: Ralph O. Meyer, Section Leader
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SUBJECT: PRIOR KNOWLEDGE OF Zr-O-U EUTECTICS

Section 19 of the staff testimony (10-26-72) for the ECCS hearings deals with reactions between Zircaloy cladding and other core materials. Eutectic formation is discussed for spacer grid materials and for alumina heater rods used in laboratory tests. Reactions of Zircaloy with UO_2 and U_3O_8 are discussed, but not in terms of eutectic formation. The general conclusion is that the extent of the reactions would be limited largely because the temperatures would be less than 2300° F, the interim LOCA acceptance criterion.

To the best of my knowledge, no further attention has been given to Zr-O-U eutectic formation in licensing work. The possibility of Zr-O-U eutectic formation was brought to our attention after the TMI-2 accident by the Fuel Behavior Research Branch, who have an exchange agreement with the Karlsruhe group, which is currently doing core-melt studies.

It should be emphasized that the temperature of formation of this eutectic (around 3500°F) is well above the 2200°F LOCA limits and, therefore, would not have been discussed in an ECCS hearing and would not be relevant to any current licensing analysis.

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19.0 FUEL ROD PHYSICO-CHEMICAL REACTIONS

This section discusses those physico-chemical interactions among the various materials of commercial light water reactor fuel rods and their immediate environment during a loss-of-coolant accident (LOCA). The zirconium steam reaction and its consequences were treated in the previous section.

The physico-chemical interactions among fuel rod cladding, UO_2, and potential environments have been studied extensively by AEC laboratories and contractors, and various vendor organizations. Included in these are: ORNL, ANL, Battelle, GE NMPO, Philips and INC. McLain has provided an extensive summary of much of this work.[19.1] In March of 1971 Idaho Nuclear Corporation (INC) (now Aerojet Nuclear Company, ANC) prepared a report, A Metallurgical Evaluation of Simulated BWR Emergency Core Cooling Tests.[19.2] This report formed the basis for much of the concern about fuel-clad-steam interaction. The authors attributed the severe cladding attack and observed temperature spikes in BWR FLECHT tests (Zr-3,4,5) to the Zr-steam reaction and a reaction between Zr and the Al_2O_3 used for heater rod insulation, followed by the subsequent formation of a Zr-Al eutectic and the reaction of this melt with steam. Supplementary tests were performed to confirm these mechanisms.[19.2] In addition, some eutectic formation was observed to have occured between the Zr tubes used in the heater rods and inconel lantern springs of the grid spacer. The temperature spikes in

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these tests were in excess of 2400°F. The authors state that the Zr-Al eutectic has a melting point of 2460°F. The severe temperature transients in these tests were initiated by the so-called "moly-shift" attributed to use of molybdenum heating elements in the simulated fuel rods.[19.3] The Zr-2k[19.4] FLECHT test, which was not considered in the ANC report,[19.2] did not exhibit the severe intermetallic attack of the other zirc tests because the kanthal heating elements were more easily controlled and the high temperatures necessary for the Zr-Al eutectic formation were not attained. Members of the Regulatory staff personally inspected the Zr-2 bundle[19.5] including the inconel lantern springs and found virtually no evidence of the attack throughout the bundle.

Because of the Zr-Al_2O_3 interaction in the Zr-3,4,5 tests which would not occur in a reactor, and the good condition of the Zr-2 bundle, the staff felt in June 1971 that this new information did not indicate a problem for light water power reactors.

Since June 1971 the Union of Concerned Scientists and the Consolidated National Intervenors have expressed concerns about eutectic related physico-chemical phenomena.[19.6,19.7]

The concerns appear to be supported and reinforced largely by recommendations for future work in the INC report on BWR FLECHT metallurgical evaluation discussed above. The entire future work section of IN-1453 is reproduced below:

"The fact that metallurgical performance anomalies such as the alumina-zirconium incompatibility can occur raises the question of what might happen in an actual ECC situation."

"As shown in Figure 23 (sample number 1) of this report, zirconium has a great affinity for oxygen at ECC conditions, since there is detectable oxygen pickup even when ZrO_2 is used as a filler material. Even though thermodynamic data do not indicate a tendency for a UO_2 reaction with zirconium, it is conceivable that irradiated UO_2 (held firmly against the tube wall by external water pressure, thermal expansion, or internal central hole pressure) which has a tendency to lose crystallinity and build up fission products (some of which migrate to the cooler regions), could give up part of its oxygen to the zirconium as an homogenization or diffusion process [13],* leaving uranium or fissium to alloy with the zirconium causing a phenomenon similar to that observed in the ECC Tests Zr-3, Zr-4, and Zr-5."

* Reference 19.17 in this section.

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"Another possibility is that tube perforation, resulting from eutectic melting caused by the lantern springs or resulting from other causes, would allow steam to come in contact with the UO_2. The UO_2 may be converted to U_3O_8 which would thermodynamically be expected to react with the Zircaloy. These possibilities bear further investigation during future work."

The following additional questions were raised:

1) Is heat release due to eutectic formation accounted for in the calculational procedures?[19.8]
2) Do the codes calculate and simulate:[19.9]
    a) Zr-Ni eutectic formation?
    b) Reaction of eutectic and steam?
    c) UO_2 + steam reaction?
    d) UO_2 + Zr reaction?
3) What evidence is there to suggest oxide inhibition of eutectic formation?[19.10]

These questions appear to have also evolved from the referenced INC report.[19.2]

The CNI testimony for the ECCS rulemaking hearing[19.6] again quotes and emphasizes the INC report Future Work Section. During questioning of the staff,[19.11] in the rulemaking hearing, CNI asked why the formation of Zr-Fe eutectic in ORNL multi-rod burst test No. 7 was not applicable to a BWR LOCA. Again, oxide inhibition of eutectic formation and computer modeling were questioned. The following sections deal with the various concerns noted above.

Reactions of Cladding and Non-Zircaloy Grid Spacer Materials

The following sub-section was suggested and prepared by ORNL in written comments to the staff.[19-12]

"Both physical metallurgy and thermodynamics must be considered in examination of the potential reactions between Zircaloy cladding and grid spacer materials. In addition, one must evaluate the significance of these reactions in light of conditions existing in a reactor during the LOCA. The following paragraphs will examine, in order, (1) reactions between zirconium and grid spacer materials, (2) the thermodynamics of the reactions and its implication, and (3) how the above relate to and are modified by the LOCA environment.

"The reaction or interdiffusion between zirconium and nickel- or iron-containing alloys in contact at high temperature can result in the formation of eutectics, intermetallic compounds, and solid solutions. Some of the eutectics formed by zirconium and nickel or iron having melting points that are several hundred degrees below the melting points of the parent metals (see table below for lowest melting Zr-Fe and Zr-Ni eutectics).

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"The temperatures calculated to occur during a LOCA are high enough for molten eutectics to form by reaction of the cladding with some grid spacer materials. Their formation could result in penetration of the cladding by the liquid and severe damage to the cladding if the reaction is sufficiently extensive.

Eutectic System	Eutectic Temperature, °F	Eutectic Composition, wt %	Range, wt %
Zr-Fe	1710	16 Fe	~ 5-55 Fe
Zr-Ni	1760	17 Ni	~ 2-25 Ni

The solid-solid reactions (e.g., compound formation) which must necessarily precede eutectic melting are important because they generate heat.

"Standard data compilations do not list the thermodynamic properties of any of the known Zr-Ni or Ze-Fe compounds (Zr_2Ni, ZrNi, $ZrNi_3$, $ZrNi_4$?, $ZrFe_2$).[19.13] However, the heats of formation of $TiNi_3$, TiNi, and Ti_2Ni are listed by Kubaschewski, Evans, and Alcock[19.14] as -33.5, -15.9, and -20.0 kcal/mole, respectively. For $ZrPt_3$, the free energy of formation, which should approximate the heat of formation, is given by Brewer[19.15] as more negative than -47 kcal/mole. Because of the chemical similarity of Ti to Zr and Ni to Pt, one should expect the reaction of Zr with Ni to be exothermic. Where data can by compared, Zr compounds are found to be more negative in their heats of formation than the Ti compounds. Therefore, the heat of formation of Zr_2Ni should be more negative than -20 kcal/mole of Ni, assuming the amount of Zr present is large, compared to the amount of nickel.

"The above indicates the approximate additional heat produced by the reactions. However, heat will be absorbed during the formation of the molten eutectic from the solid phases. The amount of heat absorbed in the melting of zirconium is approximately 5.5 kcal/mole, a value less than that of the estimated molar heat produced by the reactions. This assessment indicates that it may be important to consider the potential for these reactions to produce some net heat if they progress to an important extent.

"To form the compositions and compounds discussed above will require diffusion, a time-temperature dependent phenomenon. The cladding-grid spacer contact that exists is analogous to a solid-solid diffusion couple, and it is well known that for these couples to be effective, the surfaces of the components of the couple must be clean, smooth, and kept in intimate contact. Therefore, the diffusion-controlled rate of reaction should be complicated and retarded by the oxide films existing on the surfaces of the cladding and grid spacer materials. Some experience[19.16] indicates that when eutectic melting begins, the liquid tends to move away from the reaction site. Interruption of the contact between the grid spacer and the cladding would limit the extent of reaction."

Computer Code Simulation of Grid Spacers and Related Eutectic Formation

Some important aspects of grid spacers and eutectic formation would, if incorporated in fuel element heat up codes, lead to lower calculated temperatures results. For example, the power generation at grid spacer locations is depressed by about 5-10%.[19.17] If a grid spacer were adjacent to a hot spot and the power depression were accounted for, the peak clad temperature at the grid spacer would be about 100°F lower than presently calculated. In addition, the effect of grid spacers in the sub-channel enhances heat transfer locally. Neither the power decrease nor improved heat transfer due to the fin effects of the spacers is included in current LOCA evaluation models.

Oxide Inhibition

Westinghouse and B&W subjected Zircaloy tubes with inconel grids to steam environment for a range of conditions including those expected in a LOCA.[19.18,19.19]

In no case for which cladding temperatures were below 2200°F was cladding integrity breached due to eutectic formation. In addition, Westinghouse performed a set of similar experiments in Argon which demonstrated clearly the inhibiting effect of the oxide formation experienced in the steam tests. Photo micrographs showed that the oxide layer formed in a steam environment was very effective in preventing good contact and more rapid reaction in this diffusion controlled process.

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UO_2 - Steam Reaction

The reaction of UO_2 with steam to form higher oxides, notably U_3O_8 was studied by Baker, et al.[19.20] The authors noted that although the free energy of formation favors the reaction, very small amounts of hydrogen inhibit the reaction. A substantial amount of hydrogen would be expected to be present from the Zircaloy steam reaction. A staff calculation showed about 0.05 mol fraction of hydrogen near a hot spot at 2300°F. The authors show that even at temperatures substantially above that expected in a LOCA the kinetics of the reaction are very slow. The $Zr-H_2O$ reaction, for instance, is 10 times faster above 2000°F. Therefore, during the very short time interval during a LOCA when steam has access to the UO_2 at elevated temperatures (after rupture of the cladding), only a very small amount of oxidation could occur. The report[19.20] concludes, "The reaction of UO_2 in the presence of a reactive metal would be expected to become significant only after the metal has been completely oxidized." This could only occur after much longer exposures and higher temperatures than presently calculated for a postulated LOCA.

UO_2 and U_3O_8 Reaction with Zirconium

The thermodynamics and kinetics of the $Zr-UO_2$ reaction were explored extensively by Mallett.[19.21] Thermodynamically the free energy of the reaction is near zero so the presence of small amounts of reaction products inhibits the reaction. In fact, Westinghouse in their testimony shows the free energy to be positive. The author shows that the kinetics of reactions are indeed slow up to 2000°F. The reaction is shown as expected, to exhibit parabolic behavior and to follow a typical Arrhenius plot.

It is therefore not expected that any extensive reaction would occur even above 2000°F. The reaction of U_3O_8 with zirconium would be favored[19.2] but since the formati n of U_3O_8 is not significant neither would the reaction of U_3O_8 with Zirconium.

Furthermore, the environmental factors postulated in the "Future Work" section of IN-1453[19.2] would n be expected to exist concurrently during a LOCA. When the temperatures are postulated to be elevated for a longer period of time, the system pressure is so low that clad strain and possibly rupture due to internal pressure would prevent intimate contact of clad and most of the fuel needed for significant reaction to occur except for some small amount which might be chemically bonded and already reacted. Thermal expansion of the cladding and contraction of the fuel during a LOCA also mitigates against good fuel cladding contact. These factors which tend to separate the potential reactants in the time of concern minimize the potential phenomenon.

Reaction of Steam with Eutectic Liquid

If extensive amounts of eutectic liquid are formed, a rapid reaction with steam could occur since the mobile liquid could continually expose fresh

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metal to the steam. This has not been observed to occur except with the Zr-Al eutectic formed in Zr-3,4,5 and reported in IN-1453[19.2] at temperatures well above 2200°F. Finally, as stated in Section 19.2, the flowing liquid decouples the reaction system. This means, as shown in experiments simulating reactor fuel environment,[19.2,19.18,19.19] that little melt would form and very little reaction would occur.

ORNL Multi-rod Test No. 7

ORNL 4752[19.16] presents a qualitative description of the results of burst test No. 7 with regard to formation of eutectic. This test was non-typical since it used a stainless steel grid and was run in an Argon atmosphere. Since this test was not designed to study eutectic formation and, therefore, did not include all of the parameters necessary to evaluate the potential for eutectic reaction, its results (with regard to eutectic formation) cannot be taken as representative of the reactor situation.

The preceding comments form the basis for the Regulatory staff's opinion that potential physico-chemical reactions are sufficiently understood at this time, and do not represent a major uncertainty with respect to safety calculations. The primary concerns raised with respect to potential physico-chemical reactions (other than Zircaloy steam reactions) are those expressed by the Union of Concerned Scientists. These concerns do not appear to be shared by any of the recognized experts consulted on this matter.

In Section 18.0, Embrittlement, a temperature limit of 2200°F was suggested. If this limit is adopted, only very small amounts of zirc-nickel eutectic could form and gross melting of inconel would be precluded. The kinetics and thermodynamics of the other physico-chemical phenomena are less limiting than the zirc-steam reaction. It is, therefore, the Regulatory staff's opinion that no additional limits are required.

ORNL in their written comments[19.12] suggested numerous improvements to this report. Additionally, ORNL concurred that the various reactions considered in this chapter are unlikely to have serious effect in a LOCA.

ANC in their written comments felt that all reactions but the Zircaloy-inconel eutectic would be precluded below 2300°F.[19.22] The B&W experiments were cited.[19.19] Formulation of a time-temperature limit is recommended; however no quantitative suggestions were presented for formulating such a limit. As noted in Section 18.0, we have suggested a time-temperature limit for oxidation; however, the basis for deriving this limit did not include potential formation of Zirconium-Nickel eutectic. Our basis for believing that eutectic formation is not a problem is based on the factors discussed above.

REFERENCES FOR 19.0 - FUEL ROD PHYSICO-CHEMICAL REACTIONS

		ECCS Rulemaking Exhibit or Transcript Volume No.
19.1	H. A. McLain, Potential Metal Water Reactions in Light Water Cooled Reactors, ORNL-NSIC-23, August 1968.	95
19.2	M. J. Graber, W. F. Zelezny, R. E. Schmunk, A Metallurgical Evaluation of Simulated BWR Emergency Core Cooling Tests, IN-1433 (March 1971).	38
19.3	ECCS Rulemaking Hearing, Docket RM-50-1, Transcript page 14245.	Vol. 72
19.4	J. D. Duncan, J. E. Leonard, Thermal Response and Cladding Performance of an Internally Pressurized, Zircaloy-Clad Simulated BWR Fuel Bundle Cooled by Spray Under Loss-of-Coolant Condition. GEAP-13112, April 1971.	133
19.5	ECCS Rulemaking Hearing, Docket RM-50-1, Transcript page 4640.	Vol. 23

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		ECCS Rulemaking Exhibit or Transcript Volume No.
19.6	D. F. Ford, H. W. Kendall, James J. MacKenzie, A Critique of the New AEC Design Criteria for Reactor Safety Systems. Union of Concerned Scientists, Cambridge, Mass., October 1971.	270
19.7	Testimony of Participant Consolidated National Intervenors for ECCS Rulemaking Hearing, Docket RM-50-1, March 1972.	1094
19.8	ASLB Hearing Transcript, Consolidated Edison Company of New York, Inc., Indian Point No. 2. Docket No. 50-247, pp. 2456-7.	
19.9	ibid., pp 2382-4.	
19.10	ibid., In Camera 11-8-71, p.25.	
19.11	Reference 19.4, pp. 4640-4	Vol. 23
19.12	Trauger, D. B., Letter to D. F. Knuth Sept. 15, 1972.	

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		ECCS Rulemaking Exhibit or Transcript Volume No.
19.13	M. Hansen and K. Anderko, Constitution of Binary Alloys, 2nd edition, McGraw-Hill, 1958.	
19.14	O. Kubaschewski and C. B. Alcock, Metallurgical Thermochemistry, 4th Edition, Pergamon Press, 1967.	
19.15	Leo Brewer, UCRL-16576 (1966).	
19.16	P. L. Rittenhouse, D. O. Hobson, R. D. Waddell, Jr., The Effect of Light-Water Reactor Fuel Rod Failure on the Area Available for Emergency Coolant Flow Following a Loss-of-Coolant Accident, ORNL-4752 (Jan. 1972).	506
19.17	Wisconsin Electric Power Company, Point Beach Nuclear Plant No. 1, Start-up Test Summary, Docket No. 50-266, March 1971.	
19.18	Testimony of Westinghouse Electric Corp. for ECCS Rulemaking Hearing, Docket RM-50-1, March 1972, Appendix B.	1078

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REFERENCES (Cont.)

		ECCS Rulemaking Exhibit or Transcript Volume No.
19.19	Testimony of Donald Roy on Behalf of Babcock & Wil:ox for ECCS Rulemaking Hearing, Docket RM-50-1, March 1972, Appendix B.	1059
19.20	L. Baker. Jr., R. E. Wilson, C. Barnes, "Studies of UO_2 Steam Reaction," Chemical Engineering Division Summary Report, July-December 1963, ANL RCU-3828, May 19 6, p. 37-49.	
19.21	M. W. Mallett, "Zirc: ium-Uranium Dioxide Reaction, Chapter 7.. pp. 342-364, Uranium Dioxide, Properties and Nuclear Application, J. Belle, ed., NRDRD, USAEC, July 1961.	
19.22	ANC written comments on Chapter 19.	

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