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Rockwell
International

July 30, 1979

In reply refer to 79ESG-7531

Dr. Dale A. Powers
Office of Nuclear Reactor Regulation
Nuclear Regulatory Commission
Washington, D.C. 20555

Dear Dr. Powers:

The purpose of this letter is to document our telephone conversation of July 24 about information we may have here from the SNAP Program, that could possibly bear on hydriding of the zircaloy cladding in the Three Mile Island incident.

As I stated, the hydriding conditions in that program were substantially different from those that must have prevailed at TMI-2. To begin with, we prepared SNAP fuel by hydriding a metal rod whose surface was maintained scrupulously clean while being heated to 900°C in a vacuum furnace. The hydrogen gas used in the hydriding reaction was very carefully purified prior to admission to the furnace. I have not located any documented experience with hydriding under conditions where impurities, especially oxygen and water vapor, were known to be present. None of our own hydriding data, therefore, was obtained under conditions that match the probable situation at TMI-2: metal temperatures greater than 1500°C, the presence of H₂O and its dissociation products, and also the presence of an ionizing radiation field. However, evidence from our over 20-year-long program in hydriding technology, and relevant observations made at other sites, do show the following:

- (a) When oxygen or oxygen-bearing compounds are present in the environment surrounding zirconium or zirconium hydride, a surface layer of oxide forms.
- (b) The oxide layer is a very effective barrier to the transfer of hydrogen between the solid and the gas phases in either direction.

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Four instances of these phenomena are cited below.

(1) H₂ Loss from Zirconium Hydride in "Vacuum"

Samples of hydride (H/Zr)_{1.05} were heated in vacuum at 1150°F (620°C) and 1350°F (730°C) for 100 hours. Between 3 and 4% hydrogen was lost from the sample at 620°C, but the sample at 730°C lost essentially no hydrogen. In the latter case, the residual oxygen impurity in the vacuum rapidly formed an oxide coating on the surface that prevented hydrogen loss. A reference for this information is Report NAA-SR-8617, dated November 15, 1964, Page 1.11.

(2) Hydrogen Retention in Failed SNAP 8-ER Fuel Elements

Post-irradiation examination of the fuel elements from the SNAP 8 Experimental Reactor revealed that a substantial number had cracked cladding. These cracked elements retained hydrogen surprisingly well. The fuel composition was approximately 90 Zr-10 U (93% enriched, hydrided to a H/Zr ratio of about 1.7). Because fuel element temperatures reached peaks in excess of 850°C, it was expected that substantial hydrogen would be lost from elements with cracked cladding. Metallographic examination of such cracked elements revealed the formation of a "rind" on the surface. While this was not analyzed chemically, the conditions of operation suggested that this was an oxide layer. In order to contain hydrogen, the inside surface of the cladding and end caps had been coated with a layer of glass prior to assembly. The glass was a mixture of aluminum and barium silicates and represented a source of oxygen, which the liquid metal coolant that invaded the cracks could have carried to the surface of the fuel rod. A reference for this information is NAA-SR-Memo-12210 issued November 30, 1966, Pages 39-42.

(3) Hydrogen Loss from Zirconium Hydride as a Function of Environment Purity

Samples of zirconium hydride (H/Zr)_{1.7} were exposed for 100 hours at 600°C in the following environments: very high vacuum, very pure liquid sodium, and liquid sodium with a known oxygen impurity. Hydrogen loss from the first two

environments was a factor of about 10^6 greater than that from the impure sodium. In that sodium, an oxide coating was formed on the hydride surface that effectively prevented transfer of hydrogen. A reference for this information is the same report as in Item (2) above, Page 42.

(4) Formation of Oxide Layer on Zr Metal by H₂O Vapor Impurity

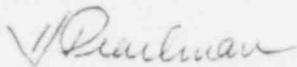
In order to eliminate the induction period for the initiation of hydriding, Zr metal is heated in vacuum at elevated temperature, prior to the introduction of hydrogen gas (see below). In one instance, the metal was heated to 1000°C, which caused desorption of H₂O from the apparatus walls, and gettering by the hot Zr. Oxidation of the surface was severe enough to prevent subsequent reaction with hydrogen. The reference for this information is NAA-SR-1508, issued October 15, 1956, Page 410.

The fact that the presence of a surface oxide layer effectively prevents hydriding of Zr metal was well known from the literature, even at the beginning of our SNAP Program. We made an exhaustive study of hydriding technology at that time, on which basis we set high standards of purity for both the metal surface and the hydrogen gas. We found that the oxide film formed even in ambient laboratory air was sufficient to impede subsequent hydriding, at temperatures of 500°C and above, in gaseous hydrogen at 1-5 atm pressure. The remedy was to preheat the metal in vacuum for several hours at temperatures up to 800°C, which diffused the surface oxygen into the bulk metal. Favorable hydriding kinetics could then be obtained, usually at 300°C, or even at lower temperatures. It is emphasized that the preheating treatment must be performed in a sufficiently high vacuum to insure a negligible chemical activity of oxygen-bearing gases (see Item 4 above). Our report, NAA-SR-1508, is also the reference for the above information. This 834-page document, which lists 848 references, contains a thorough discussion of the fundamental studies on the Zr-H system by Dr. Earl A. Guibransen and his colleagues. It includes a detailed evaluation of the effects of surface oxide layers on the kinetics of hydriding. In none of these studies was the initial oxide surface replenished. Contrariwise, conditions at TMI-2 seem to have been very favorable for replenishing an oxide surface layer.

79ESG-7531
July 30, 1979
Page 4

I believe that hydriding of the core cladding at TMI-2 could not occur to any significant extent. If you have questions about this or any other aspect of this letter, please do call me at (213) 341-1000, Extension 2233.

Sincerely,



H. Pearlman, Manager
Materials and Physics Technology
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klp:727

cc: Dr. W. V. Johnston, Chief
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