SHEAR-LEACH PROCESSING OF N-REACTOR FUEL--
CLADDING FIRES

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ABSTRACT

Cladding fires which occurred in 1967 and 1968 during shear-leach processing of irradiated N-Reactor fuel (Zircaloy-clad uranium) at the Nuclear Fuel Services, Inc., West Valley, New York, facility are described. Limited laboratory investigations suggest that these fires either occurred or, at least, were triggered when HNO_3 -sensitized weld beads on the ends of fuel rods ignited (by mechanical shock) and burned. Beryllium in the weld Zr-Be system is preferentially attacked in HNO_3 solutions. A sensitized zirconium metal matrix results which, when shocked electrically or mechanically, detonates in air with a loud report and a brilliant white flash. Insufficient data were obtained to establish if detonation of sensitized weld beads would ignite sheared Zircaloy cladding fines, U-Zr alloy in the diffusion zone between cladding and core, or hydrided cladding.

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SHEAR-LEACH PROCESSING OF N-REACTOR FUEL-- CLADDING FIRES

INTRODUCTION

Shear-leach processing of irradiated, N-Reactor fuel (Zircaloy-clad uranium metal) was performed on a campaign basis from 1966 to 1971 at the Nuclear Fuel Services, Inc., (NFS) plant in West Valley, New York. On several occasions in 1967 and again in 1968 leached cladding hulls ignited and burned. Some of the fires occurred when the hulls were dumped from the perforated baskets used to contain sheared fuel into steel bins; in these cases, the ignited hulls were reported to glow like a "bed of charcoal."^[1] Additional fires occurred in the dissolver vessels as evidenced by 10- to 12-inch diameter holes burned through the one-quarter-inch thick basket wall.

Such fires were not observed during processing of Dresden Reactor Zircaloy-clad UO_2 fuel. Their occurrence with N-Reactor fuel was completely unexpected from previous technology and prompted low-level research efforts in 1968 and 1969 both at Hanford and at Oak Ridge National Laboratory (ORNL) to determine their origin. Motivating the Hanford effort also was the consideration then being given to a crush-leach scheme for processing N-Reactor fuel in the Hanford Purex plant. Plans to implement this processing scheme were subsequently dropped* and along with them incentive and funding for continuation of our studies of the causes and mechanisms of cladding fires, unfortunately before such studies were complete.

* The aqueous Zirflex process^[2] is currently used in the Hanford Purex plant to remove Zircaloy cladding from N-Reactor fuel.

Nevertheless, it is believed worthwhile to recapitulate observations made by NFS personnel and to report formally what progress was made at Hanford and at ORNL in assessing various hypotheses about the cause(s) of cladding fires. Such documentation is particularly appropriate now when plans are being made to return to Hanford those N-Reactor elements still remaining at the NFS West Valley facility. This report may also be helpful in evaluation of fuel types suitable for possible extended (beyond 1974) operation of the N-Reactor.

SUMMARY AND CONCLUSIONS

Described here are the cladding fires which occurred at the NFS West Valley plant in 1967 and 1968 during shear-leach processing of Hanford N-Reactor fuel. [A detailed account of these fires has not been published heretofore.] Limited literature and laboratory investigations were performed to determine the cause of these fires; principal focus of the report is on the results of these studies.

Evidence presently available indicates these fires either occurred or, at least, were triggered when HNO_3 -sensitized weld beads on the ends of fuel rods ignited, by mechanical shock, and burned. Beryllium (or, possibly an intermetallic ZrBe_4 compound) in the weld Zr-Be system is preferentially attacked in HNO_3 solutions. A sensitized zirconium metal matrix results which, when shocked electrically or mechanically, detonates in air with a loud report and a brilliant white flash. Weld bead fires do not propagate to the Zircaloy cladding and leave no ash or other residue when extinguished.

Sensitized weldments will not detonate either in a vacuum or in an inert atmosphere containing less than about 5 vol% O_2 . [In Ar-5 vol% O_2 sensitized welds "burn" with an orange glow.] In two tests, sensitized welds were immersed for five minutes in 5M NaOH solution; the resulting fuel pieces could not be

detonated even after drying in air for 30 minutes. Caustic dipping was employed on an empirical basis at West Valley to prevent fires during disposal of leached N-Reactor fuel cladding hulls.

Except for end section weld beads, N-Reactor cladding is inert to HNO_3 . Test fuel specimens and components examined in this work included inner and outer cladding surfaces on both unirradiated and irradiated fuel sections; brazed end closures prior to welding; Zr-5 wt% Be braze rings; hydrided Zircaloy cladding; and autoclaved, defected fuel pieces simulating ruptured fuel elements. Pyrophoric surfaces were not present on any of these latter specimens before, after, or during immersion in boiling HNO_3 . These observations imply very strongly that NFS cladding fires represented only combustion of sensitized weldments. However, the possibility that detonation of sensitized weld beads ignited sheared Zircaloy cladding fines, U-Zr alloy in the diffusion zone between cladding and core, or hydrided cladding cannot be ruled out completely by available data.

In the latter connection, the very limited nature of the experimental effort is emphasized. Recommendations for additional work, particularly with end sections from irradiated fuel, are made.

N-REACTOR FUEL MANUFACTURING PROCESS

Zircaloy-2 clad uranium metal N-Reactor fuel is of a "tube-in-tube" design. Outer diameters of the outer and inner tubes are 2.425 and 1.279 inches, respectively; while inner diameters are 1.701 and 0.480 inches, respectively. The fabrication process which is performed for both inner and outer N-Reactor tubes is shown graphically in Figure 1 and summarized in Table I. This particular end closure scheme which employs a Zr-Be braze ring is unique to N-Reactor fuel.

FIGURE 1

TABLE I
N-REACTOR FUEL FABRICATION STEPS

1. Coextrude uranium metal and Zircaloy cladding.
2. Cut extruded pieces to fuel element length (26 inches).
3. Machine uranium out of ends of fuel lengths.
4. Complete removal of uranium from fuel element ends by chemical milling with $\text{HNO}_3\text{-H}_2\text{SO}_4$ solution.
5. Put in Zircaloy-2 end caps.
6. Put in Zr-5 wt% Be braze rings.
7. Braze under vacuum at a temperature above 1000 °C.
8. Heat-treat by immersion in a molten salt bath at 720 to 750 °C.
9. Quench at 300 °C.
10. Machine for end cap closure.
11. Weld ends.

NFS EXPERIENCE WITH N-REACTOR FUEL

A description of the NFS cladding fires has not been published heretofore. That given here is based on information gleaned from telephonic conversations held in the period 1968 to 1972 between J. P. Duckworth, NFS, and various persons at Hanford and ORNL; from my visit to the NFS West Valley plant in May 1968; and from the visit of J. P. Duckworth to Hanford in 1970.

SHEAR-LEACH EQUIPMENT AND PROCEDURES

At the NFS plant, N-Reactor fuel was sheared in argon into about one-inch-long sections using shear equipment and technology developed at ORNL.^[3] The outer torus of the fuel was

crushed by the shear, but the inner fuel sections broke cleanly without either crushing or without production of feather cladding edges observed when unirradiated fuel was sheared (see page 11).

At least three (perhaps more?) of the fires occurred during a period of improper shear operation; tearing and production of more fines than usual was reported. Measurements made at ORNL in the Spring of 1968 with 3 kg of NFS-sheared N-Reactor fuel showed that about 64% of the material would pass through a 4-mesh screen.

Sheared fuel was contained in stainless steel baskets, 8-inch diameter by 9-feet long, having one-eighth-inch perforations and 5.5% free area. Each basket was fitted with a 10-mil thick mild steel liner to prevent cladding and fuel fines from falling out while transporting the fuel to the dissolver. The consumable steel liner and uranium were dissolved (in two cuts) in HNO_3 containing a small amount of $\text{Hg}(\text{NO}_3)_2$ to suppress volatilization of ^{131}I . The initial HNO_3 concentration of the dissolvent varied, as discussed later, with exposure level of the fuel.

Following dissolution, leached zirconium hulls were removed from the dissolver in the perforated baskets and dumped, by means of a dumping rack, into metal bins. [These bins are about two-feet square by one-foot high with a tapered bottom.] An argon purge of the bin was maintained during the dumping operation although the rest of the hot cell was operated with an air atmosphere. The bins were later dumped into 30-gallon drums for disposal of the cladding; barrels of cladding were argon-purged during normal plant storage.

N-REACTOR FUEL PROCESSING HISTORY

Pre-Fire Experience

Processing of N-Reactor fuel at the NFS plant began in

April 1966. The history of the first five months' operation is documented in Reference 4. During this period two cuts with 11 to 12M HNO₃ were used to dissolve fuel with an average exposure less than 1000 MWd/tonne. Although several dissolver pressurizations occurred, no fires were observed.

Cladding Fires in 1967-1968

The best information currently available indicates 19 fires occurred in 1967 and 1968 during processing of fuel with exposures in the range 1000 to 4000 MWd/tonne. Of these, 14 occurred in the dissolvers, four occurred in the bins during or shortly after the dumping operation, and one minor fire occurred when one or two pieces of cladding fell from a basket onto the canyon deck.

Bin fires had the appearance of burning charcoal; the cladding surface glowed red with an occasional small flame, say an inch high. All the bin fires were extinguished with solid NaCl; the longest burned about 15 minutes before being extinguished. Significantly, no visible ash or other evidence of combustion was ever detected after fires were extinguished. Although no explosions were observed, severe sparking of the hulls was noted when they were poured from the baskets into the bins. According to NFS observers, sparking was much more pronounced with N-Reactor hulls than with Dresden Reactor hulls.

Dissolver fires were not observed directly but were evidenced by 10- to 12-inch diameter holes burned through the one-quarter inch thick basket wall. In all instances these fires occurred in the upper portion of the basket. In two cases the dissolver vessel itself was damaged sufficiently that it had to be removed from service. Several, but apparently not all, the dissolver fires occurred shortly after fuel dissolution started.

Following the fourth bin fire, leached hulls were routinely

dipped in aqueous caustic.* Thereafter, as far as can be determined, only one other fire occurred with the leached hulls. In this case the leached hulls, after dipping in caustic, were allowed to dry out before dumping. One or two hulls fell from the basket and caught fire and glowed briefly when they struck the canyon deck. The remaining hulls were redipped in caustic and dumped without ignition.

Significant changes were also made in the fuel dissolution regime which prevented further dissolver fires. These included segregation and non-processing of ruptured fuel (see the later discussion); lowering the height of the fuel in the basket; and decreasing initial dissolvent acidity to compensate for the increased dissolution rate of highly irradiated N-Reactor fuel.[†] As indicated earlier, for fuel irradiated to about 1000 MWd/tonne the initial dissolvent was 11 to 12M HNO₃; no control problems were encountered in this case. For 1000 to 3000 MWd/tonne fuel the initial dissolvent acidity was dropped to 9M; in this case very rapid dissolution occurred even with cooling water in the dissolver steam coils! Adequate control of the dissolution at this and higher fuel exposures was achieved by charging the fuel into water and then adding 3M HNO₃ to initiate dissolution.

Post-Fire Experience

Utilizing preventive measures developed in 1968, further

* The decision in 1968 to dip leached hulls in aqueous NaOH was apparently an Edisonian hunch which, as later experience showed, paid off handsomely. Indeed, when asked why caustic dipping was started, one NFS executive replied, "What would you have done?"

† That neutron irradiation significantly increases the rate at which uranium metal dissolves in HNO₃ is well known from previous laboratory studies. This effect results from micro-cracking and other mechanical stresses which greatly increase the area of metal exposed to the HNO₃ dissolvent.

processing of N-Reactor fuel in 1969, 1970, and 1971 was accomplished without occurrence of fires.

RUPTURED FUEL ELEMENTS

N-Reactor fuel was shipped from Hanford to West Valley in a water-filled cask. When received at West Valley, the fuel elements were loaded under water into aluminum canisters and stored under 12 feet of water until ready for processing.

According to Douglas United Nuclear Company personnel at Hanford, only unruptured N-Reactor fuel elements were shipped to West Valley. Yet, in their fuel examination (shear) cell NFS personnel observed, per 30 tons of fuel, 5 to 10 ruptured elements for 1000 MWd/tonne material and as many as 60 to 70 ruptures for 3000 MWd/tonne elements. Only the outer torus of the N-Reactor fuel ruptured; inner sections remained intact. Ruptured elements contained a finely divided black powder--presumably UO_2 produced by the reaction:

Fuel ruptures which occurred in the NFS basin reflected, presumably, cladding defects induced by mechanical stresses experienced during the overland journey from Hanford to West Valley.

Unprocessed, ruptured N-Reactor fuel elements are currently being held at the NFS plant pending shipment back to Hanford.

EXPERIMENTAL

MATERIALS

Unirradiated N-Reactor Fuel Pieces

Some of the unirradiated N-Reactor fuel specimens used in this work are pictured in Figure 2. Most of the tests were

FIGURE 2
UNIRRADIATED N-REACTOR FUEL TEST PIECES

performed with one- to two-inch-long sections cut from the ends of welded, production-type inner N-Reactor fuel elements (Type 2, Figure 2); some of these (Type 1) were split longitudinally to expose the inner surface of the weldment. Fuel element types 3, 4, and 5 were all cut from the end of clad, capped, and brazed but unwelded production-type inner N-Reactor elements. Type 3 pieces were machined for final welding, while Types 4 and 5 were not so machined. Types 4 and 5 differed only in the length of uranium metal core attached to the end cap--about one inch for Type 4 and less than one-sixteenth inch for Type 5. Both heat-treated (heat at 730 °C) and non-heat-treated Type 4 and 5 pieces were procured.

In addition to the test pieces pictured in Figure 2 some experiments were performed with two-inch-long sections cut from the middle of inner N-Reactor elements. Cladding was intact except at the ends.

Sheared, nonirradiated N-Reactor fuel was obtained from ORNL. Sheared material from ORNL consisted of about one-inch-long pieces with inner and outer fuel sections still joined. With unirradiated fuel, the shearing operation wiped the cladding inward across the uranium core for a distance of about one-sixteenth to one-eighth inch, leaving a fine feather edge of Zircaloy cladding. This edge was irregular and very thin (perhaps 0.005-inch thick) with very little physical strength.

Irradiated N-Reactor Fuel Specimens

Pie-shaped pieces weighing 20 to 30 grams were cut from the outer surface of three irradiated inner N-Reactor elements. Zircaloy cladding was intact on the curved portion of these specimens. Test specimens were cut from typical low, intermediate, and high exposure fuel elements; specific exposure levels are not quoted here to avoid classification problems.

None of the test pieces were cut from the welded ends of the fuel elements.

Special Welded N-Reactor Fuel Pieces

Several special 1- to 1 1/2-inch-long N-Reactor fuel sections with welded Zircaloy end caps at each end were prepared for use in autoclave tests to simulate in-reactor rupture of defect fuel elements. These specimens were fabricated from a single completed but not autoclaved production N-Reactor fuel element. The fuel element was cut into appropriate lengths, faced, and machine-recessed to within 0.010-inch of the cladding walls. Chemical milling was used to remove final traces of uranium from the cladding walls and to reach final depth. Zircaloy-2 ends (one-quarter-inch thick) were electrobeam-welded (without use of Zr-Be alloy braze rings) in place to form unbonded closures. The ends of the original fuel elements were used for two of the special pieces; these pieces had production-type bonded closures on one end. The final welded shapes were heated in vacuum for 100 hours at 300 °C and then autoclaved for 48 hours at 400 °C (1500 psi steam).

Holes--0.026-inch diameter by 0.065-inch deep--were drilled in the center of these special welded fuel pieces. These holes were deep enough to penetrate through the cladding to the uranium metal. The defected fuel pieces were autoclaved in 250 °C water (1500 psig) for 4.5 hours. Rupture behavior followed the typical pattern described in Reference 5. Approximately 140 grams of uranium were oxidized to UO_2 .

Braze Rings

When these studies were completed (1969) two types of Zr-5 wt% Be braze rings were used in fabrication of inner N-Reactor fuel. One type (Whittaker Corporation, West Concord, Connecticut) was made by a casting process while the other type (NUMEC, Apollo, Pennsylvania) was made by a powder metallurgy process.

Samples of each type were procured; chemical analysis of these rings is listed in Table II. Each ring was about 0.25-cm thick and weighed about 9 grams.

TABLE II
CHEMICAL COMPOSITION OF BRAZE RINGS

<u>Element</u>	<u>Cast Type</u>	<u>Powder Metallurgy Type</u>
Be, wt%	5.10	4.98
O, ppm	614.	1820.
C, ppm	441.	256.
H, ppm	0.8	65.
N, ppm	59.	93.

Hydrided Zircaloy Cladding

Conditions used to hydride a 2-inch-long section of Zircaloy-2 cladding (after HNO₃ dissolution of the uranium) from a production N-Reactor inner fuel element were as follows:

Temperature:	400 °C
Initial H ₂ pressure:	84 torr
System volume:	1.53 liters
Hydriding kinetics:	9 min - 50% reaction 30 min - 100% reaction
Hydriding level:	~2100 ppm
Terminal Solubility at 400 °C:	~200 ppm

Hydriding was nonuniform since some fines (ZrH₂?) were present at the end of the reaction. These fines apparently resulted from massive hydriding of the cladding at one end.

Other Materials

Argon-oxygen mixtures containing 3, 5, 7.5, and 12 vol% O₂ were obtained from the Air Reduction Company; ultra-pure

oxygen and argon were used to prepare these mixtures. All other chemicals were of reagent grade quality.

PROCEDURES

Nitric Acid Sensitization Procedures

A wide spectrum of HNO_3 solutions and procedures was used in attempts to sensitize N-Reactor fuel specimens. Type 2 (Figure 2) pieces were immersed for 17 hours in about 500 ml of boiling 9M HNO_3 . These conditions sufficed for complete dissolution of the uranium [to produce $\sim 1M$ $\text{UO}_2(\text{NO}_3)_2$ solutions] and for sensitization of the weldment on the end of the test piece. Ordinarily, undissolved cladding sections were removed from the HNO_3 solution after 17 hours, dried in air for about 5 minutes, and tested for sensitive areas. In some cases HNO_3 -treated cladding sections were dried in air for 24 hours; and, in some cases, they were rinsed with either water or 5M NaOH before drying in air. Terminal dissolver solutions produced in several experiments were analyzed for beryllium and zirconium by atomic absorption methods.

With only minor modifications in initial HNO_3 concentration and volume, the sensitization procedure used with Type 2 pieces was also followed with the other fuel specimens shown in Figure 2.

Two-inch-long sections cut from the middle of inner N-Reactor fuel pieces were treated with excess boiling 15.6M HNO_3 to dissolve all the uranium and produce $\sim 1M$ $\text{UO}_2(\text{NO}_3)_2$ - $\sim 2M$ HNO_3 solutions. Periodic checks were made both during and after the dissolution step for presence of sensitive surfaces.

Special welded N-Reactor fuel pieces (page 12) were mechanically defected and autoclaved as described earlier. The resulting material-- UO_2 plus unreacted metal--was completely dissolved in boiling 12.2M HNO_3 . The cladding section

remaining after this treatment was air-dried and tested for reactive surfaces.

Irradiated N-Reactor fuel pieces were completely dissolved in excess 12.2M HNO_3 to yield solutions approximately 0.2M $\text{UO}_2(\text{NO}_3)_2$ and 11M HNO_3 . Periodically, dissolving pieces were removed, dried in air, and checked for sensitive surface and/or materials. Zircaloy cladding remaining after uranium dissolution was complete was also removed, dried in air, and tested for the presence of sensitive surfaces.

In attempts to sensitize hydrided Zircaloy cladding and Zr-5 wt% Be braze rings the former was immersed for 3 to 4 hours in boiling 11M HNO_3 , while braze rings were boiled for an hour in 12.2M HNO_3 .

Ignition of Sensitized Fuel Pieces

Sensitized surfaces on various test uranium and cladding specimens were conveniently ignited by the spark from a high-voltage discharge Tesla coil. This ignition method proved very reliable and had been used previously to detonate HNO_3 -sensitized U-Zr alloy surfaces.^[6] Ignitions tests were ordinarily performed in air with the operator protected from sparks, etc., by adequate safety shields and safety clothing.

The simple apparatus depicted in Figure 3 was used to study ignition of sensitized pieces in vacuum and in Ar- O_2 atmospheres. In the latter case the system was thoroughly flushed with the appropriate Ar- O_2 mixture before ignition.

RESULTS AND DISCUSSION

SENSITIZATION OF WELDS ON END CLOSURES

Weld beads and surfaces on the ends of unirradiated N-Reactor fuel elements readily sensitize when exposed to boiling HNO_3 solutions. Nuclear Fuel Services cladding fires,

FIGURE 3

APPARATUS FOR IGNITION OF SENSITIZED TEST PIECES

both in hull bins and in dissolvers, are believed to have resulted from, or at least were triggered by, ignition (mechanical shock) and combustion of such sensitized areas.

Sensitized weld areas, when shocked electrically in air, detonate with a brilliant white flash and a loud report like a firecracker. Typical detonations are shown in Figure B-1 (Appendix B); note particularly the "Saturn V-type" ignition pictured in the lower left corner. For comparison, action of the Tesla coil discharge on unsensitized weld beads is shown in Figure B-2.

Other pertinent observations are:

1. Aside from the weldments, none--absolutely none--of the other test specimens shown in Figure 2 or otherwise described on pages 11-13 could be sensitized by boiling HNO_3 .
2. In two tests sensitized welds were immersed for five minutes in 5M NaOH at 25 °C; the resulting fuel pieces could not be detonated even after drying in air for 30 minutes. Similar behavior was noted in one experiment where the sensitized piece was dipped in water for five minutes. [In one of the tests with NaOH solution one section of the sensitized fuel piece was detonated (see Item 4 below) prior to immersion in the NaOH solution to prove that sensitized surfaces were indeed present.]
3. Sensitized weld surfaces will not ignite in a vacuum or in an inert gas containing less than about 5 vol% oxygen. These surfaces "burn" with an orange glow in argon containing 5 vol% oxygen (Figure B-3); combustion is much less vigorous in this atmosphere than it is in air.
4. With Type 1 (Figure 2) fuel sections sensitized weld beads around the inner hole and on the outer surface

can be ignited separately. Sensitized areas on Type 1 fuel pieces which can be detonated separately include the welded faces on the cut portion as well as the inner and outer weld beads.

5. When sensitized weld beads on Type 2 end pieces are ignited the resulting fire usually quickly traverses the circular weld bead and ruptures it. Weld bead fires do not, however, propagate to the unsensitized Zircaloy cladding on either Type 1 or Type 2 fuel pieces. Also, no residues or ashes are produced by combustion of the sensitized weld areas.

Although discovered independently in this investigation, sensitization and ignition of weld areas on N-Reactor fuel was observed as early as 1965. Hudson in a memorandum dated June 11, 1965, describes sensitization of weld beads by chemical milling solution (an $\text{HNO}_3\text{-H}_2\text{SO}_4\text{-CuSO}_4$ solution) and subsequent ignition by mechanical shock; the full text of Hudson's memo is reported in Appendix A. Hudson suggested that the chemical milling solution preferentially dissolved beryllium from the weld Zr-Be alloy leaving a spongy, sensitized zirconium matrix.* This same explanation also accounts for sensitive surfaces generated in this study by exposure of weld metal to boiling HNO_3 . However, admittedly meager analytical data show beryllium and zirconium to both be present in the final HNO_3 solution in the mole ratio 4Be:Zr. These data suggest that HNO_3 solutions preferentially dissolve an intermetallic compound of composition ZrBe_4 from the weld alloy. The constitutional diagram for the Zr-Be^[7] system shows an intermetallic ZrBe_2 compound but not a ZrBe_4 compound.

* Hudson states that porous black surfaces were formed when weld alloy was exposed to chemical milling solution. Such black surfaces were not observed in this work.

Generation of sensitized weld beads and their subsequent ignition is believed, as stated in the introduction to this Section, to account for NFS cladding fires. Properties of sensitized weld alloy, especially its desensitization by NaOH solution and the absence of a residue after burning, correspond very closely to those observed during NFS bin fires. Mildly disconcerting is our failure to produce prolonged (~15 minutes) "glowing charcoal" cladding fires. Combustion of sensitized weld alloy in a limited supply of oxygen (Figure B-3) approached this type of fire, however, It is also possible that sensitized weldments on irradiated fuel burn differently than those on unirradiated fuel; behavior of weld metal on end closures of irradiated fuel was not determined in this work. Finally, it is also possible that detonation of sensitized welds in the NFS bins ignited sheared Zircaloy-cladding fines, U-Zr alloy in the diffusion zone between cladding and core, or hydrided cladding.

Quantitative measurements of the energy released by detonation of sensitized weld alloy were not made. Qualitative observations (Figure B-1) suggest near-simultaneous detonation of sensitized welds on several sheared end pieces would release sufficient energy to burn a hole in a perforated NFS fuel basket. In connection with the NFS dissolver fires, Duckworth states^[1] that rapid release of nitrogen oxides from dissolving highly irradiated uranium metal (and, perhaps, the mild steel liner) may have created a sort of "fluidized bed" in the perforated baskets. Under these conditions sheared fuel pieces at the top of the basket would likely be in the vapor space and would be colliding with one another. Such collisions could provide the initial mechanical shock needed to detonate sensitized welds. In this theory of NFS dissolver fires, weld beads presumably sensitized either during the very early part of the dissolution or, more likely, in first of the two dissolution cuts. Unfortunately, it is not known if all

the dissolver fires occurred during the second cut.

ALTERNATIVE HYPOTHESES FOR ORIGIN OF CLADDING FIRES

Although NFS cladding fires are currently thought to have most likely been caused by combustion of sensitized weld alloy, from time to time various other explanations for these fires have been put forth. These alternative hypotheses are considered in this Section.

Ignition of U-Zr Alloy Diffusion Zone

Uranium metal diffuses into the Zircaloy cladding during N-Reactor fuel manufacture. [According to ORNL measurements^[8] unirradiated, HNO₃-leached hulls contain about 0.05 wt% uranium.] The U-Zr alloy system including, at least in irradiated fuel (see the discussion below) the epsilon phase, an intermetallic compound of composition either UZr₂^[6] or UZr₃,^[9] is established in the diffusion zone. The highly pyrophoric nature of the epsilon phase which is left as a finely divided black residue when U-Zr alloys containing less than about 30 wt% Zr dissolve in HNO₃ is well known.^[6,9,10] It is not surprising, therefore, that ignition of epsilon phase material should have been the first explanation advanced to account for NFS fires.

This hypothesis is not supported by the available experimental evidence. In tests at both Hanford and ORNL, exposure of the diffusion zone in the inner cladding surface of irradiated fuel pieces to HNO₃ repeatedly failed to generate either any epsilon phase residue or any other kind of sensitized material. These tests do not completely rule out the possibility that detonation of weld alloy could ignite the diffusion zone itself, however.

The constitutional diagram for the U-Zr system^[11,12] shows that the epsilon phase is stable at room temperature

but disappears completely at temperatures above 607 °C. Hence, the epsilon phase is not present in the diffusion zone in unirradiated N-Reactor fuel which has been heat-treated at 720 to 750 °C and quenched at 300 °C (see Table I). The epsilon phase would be expected to be present in irradiated fuel which is heated to a temperature less than 607 °C during reactor exposure. To my knowledge, however, direct confirmation of this latter expectation has not been made. Working with freshly leached, irradiated cladding hulls Richt at ORNL tentatively identified (by X-ray diffraction) the thin layer which remained on the surface of the cladding at the original uranium-zirconium interface as $U_{0.6}Zr_{2.4}$.^[13] The relationship, if any, of this material to the epsilon phase is not known.

Ignition of Uranium and/or Zirconium Hydrides

Attempts have been made to correlate the occurrence of the NFS fires with the increase in number of ruptured fuel elements processed in 1967 and 1968 (see page 9).^{*} The dissolver fires, in particular, may have occurred, it has been suggested, from reaction of HNO_3 with UH_3 . The latter compound is formed during the fuel rupturing process as an intermediate in the reaction of uranium metal with water or steam^[5] and is well known to react explosively with oxidizing agents.^[14] Extension of the "hydride hypothesis" to the bin fires is more difficult, but it is conjectured these might have occurred from combustion of either hydrided Zircaloy cladding or, possibly, hydrided diffusion zone U-Zr alloy. Hydriding of Zircaloy cladding components during N-Reactor fuel element rupture is discussed by Troutner.^[5]

* There is no way of knowing with certainty now, four years later, that the fires occurred only when processing ruptured fuel.

Our tests of the hydride hypothesis were limited to one experiment with hydrided cladding (page 13) and to several experiments with defected, autoclaved fuel pieces simulating ruptures (page 12). Except for the weld beads on some of the latter pieces, no sensitized surfaces were produced in any of these tests. Obviously, the hypothesis that the NFS fires resulted from combustion of hydrides cannot be rejected outright on the basis of the results of such limited testing. Still, it is difficult to understand on this hypothesis why dissolver fires should have been confined only to the upper portion of the perforated fuel baskets. Also, there is no evidence at all to indicate that hydrided cladding and hydrided U-Zr diffusion zone, even if present, will ignite and burn.

Ignition of Feather Edges on Sheared Cladding

As mentioned previously (page 11), feather edges of Zircaloy cladding are wiped across the uranium metal surface during shearing of unirradiated N-Reactor fuel. An early hypothesis (advanced by C. D. Watson at ORNL) to account for the NFS cladding fires was that these feather edges somehow ignited (perhaps from sparks generated during dumping of the hulls into storage bins) and burned. This hypothesis proved untenable when it was established that brittle, irradiated N-Reactor fuel shears sharply and cleanly without production of feather edges of cladding.

For the record, feather edges of cladding on unirradiated sheared cladding will burn if ignited. To establish this fact, several sheared fuel sections containing feather edges of cladding were exposed to fresh portions of boiling 12M HNO_3 to dissolve all the uranium. Needles of cladding produced during the shearing process were also immersed in boiling 12M HNO_3 to remove uranium. Subsequently, cladding needles and sheared sections were dried in air and positioned randomly on

a raised stainless steel screen in a heated (90 °C) small steel tray. All the feather edges and a few of the fines ignited and flared briefly with an intense white glow when exposed to the discharge of the Tesla coil. In no case, however, did the fire propagate to the bulk cladding.

RECOMMENDATIONS FOR ADDITIONAL WORK

Complete characterization of NFS cladding fires was not possible within the scope of available funding and time.

Recommended areas for further study include:

1. Sensitization and ignition (in both air and in Ar-O₂ mixtures) of weld alloy on end closures of irradiated fuel. Desirably, these studies should be done with sheared fuel pieces.
2. Characterization of sensitized weld alloy, both before and after ignition, by electron probe analyses and other metallurgical techniques.
3. Determine the energy released by combustion of sensitized weld alloy.
4. Determination of the mechanism whereby water and NaOH solutions passivate sensitized weld surfaces.
5. Under conditions simulating NFS dumping of leached hulls into storage bins determine if detonation of sensitized welds will ignite either sheared cladding fines or U-Zr alloy in the inner cladding surface.
6. Determine HNO₃ dissolution behavior of sheared, ruptured N-Reactor fuel.

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APPENDIX A:

ZIRCALOY SURFACE EXPLOSIONS ON N-FUEL WELD SAMPLES

W. G. Hudson, June 11, 1965

Following is the text of a memorandum entitled *Zircaloy Surface Explosions on N-Fuel Weld Samples* prepared on June 11, 1965, by W. G. Hudson of the General Electric Company.

"A recent incident involved surface explosions occurring on sample specimens of welded, brazed N-fuel end closures in the Pilot Plant. This was the first reported incident of this type since the startup of fuel development and fabrication. A review of the literature on sensitized zirconium and how it is formed was made to provide an explanation of this incident. Most of the literature deals with explosions occurring with finely divided zirconium or zirconium uranium alloys. In the case of the finely divided or sponge zirconium, a high surface to mass ratio exists. When this type of surface is exposed to conditions of heat, flame, or shock of sufficient intensity, a reaction occurs (burning) which proceeds at an explosive rate. There are many theories as to the actual mechanism which produces this effect, none of which have been universally accepted. In any case, the effects and general causative factors have been recognized and accepted. In the case of the subject incident, the problem at hand was to determine the nature of the sensitized surface and how it occurred.

"The weld area of a brazed fuel contains on an average of 1 to 2 per cent beryllium as an alloy. This may be compared to zircaloy alloyed with uranium to this extent. The latter is known to be explosive when etched in acid which preferentially dissolves uranium (e.g., HNO_3) leaving a spongy unoxidized zircaloy matrix.

"With this background information, the following summary of events are presented with conclusions as to the cause of the described incident.

- "1. Fairly early in the fuel production it was observed that exposure of fuel welds to the chemical milling solution, a mixture of HNO_3 , H_2SO_4 and CuSO_4 , produced a porous black surface indicating a reaction occurred between probably beryllium and the nitric sulfuric acid mixture. This was verified in lab tests by observing the generation of reaction gases which produced bubbles at the weld surface but not on the other zircaloy clad surfaces. The preferential dissolution of beryllium probably left a spongy zirconium as in the case of the action of nitric acid on uranium zirconium alloys which leave a spongy zirconium matrix with explosive sensitivity.

- "2. The explosive sample specimens were exposed to chemical milling solution for 7 or 8 hours in order to dissolve out the uranium for offsite transport of the uranium-free end closure specimen. This was the first time to anyone's knowledge that this type of preparation has been performed on end closure sample specimens.
- "3. Subsequent handling and polishing of the specimens resulted in the two surface explosion incidents.
- a. When the specimen was polished on the wet sander, the weld bead ignited with a white flash burning around the weld and exposed braze surfaces.
 - b. A specimen was dropped on the concrete floor, exploded with a white flash accompanied by a noise similar to a firecracker exploding. The burned surfaces were around the weld surface and on the exposed braze surfaces.

"Since the samples involved were done in the Pilot Plant facility, some consideration was given to the possibility of solution characteristic as a factor in producing the surface sensitivity.

"A set of samples was processed in both the 333 production solution and in the Pilot Plant solution at the same time. The samples were then exposed to sparking by filing. Although they were very pyrophoric leaving trails of burning sparks with each scrape of the file, they did not burn the length of the weld area as in the original incident. Since the original samples were wet when the incident occurred, the test samples were subjected to the same mechanical treatment when wet. The samples prepared in the Pilot Plant solution ignited and burned the weld areas as in the original incident. The production solution samples, although evidencing increased pyrophoricity when wet, did not ignite spontaneously on the weld areas.

"The Pilot Plant and production solution differed primarily in their dissolved uranium content. Also the residence time in the production solution was approximately two hours less than those in the Pilot Plant solution.

"About the only recommendation which can be made at this time is to publicize this incident so that if any future need for uranium free end closure samples arises, the work can be done safely. After the subject incident occurred, the balance of the required samples were chemically milled with the weld and braze area protected by fiber glass mountings.

"Presently, rework production fuels are chemically milled with one welded end immersed in the milling solution. Residence time in this case is about 20 minutes. This is insufficient to give a zircaloy sponge of sufficient thickness for explosion sensitivity."

(Signed)
W. G. Hudson
N-Fuels Engineering

APPENDIX B:

PHOTOGRAPHS OF WELD FIRES

B-1

ARH-2351

FIGURE B-1
IGNITION OF SENSITIZED N-REACTOR FUEL WELDS--
TYPICAL VIEWS

B-2

ARH-2351

FIGURE B-2
TYPICAL NONIGNITION OF INERT N-REACTOR
FUEL TEST PIECES

FIGURE B-3
IGNITION OF SENSITIZED WELD IN Ar-5 vol% O₂

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