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CORROSION EVALUATION OF N REACTOR PRESSURE TUBE 1756

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A. P. Larrick

Surface and Coolant Chemistry Section

CHEMISTRY AND CHEMICAL ENGINEERING DEPARTMENT

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CORRESION EVALUATION OF N REACTOR PRESSURE TUBE 1756

A. P. Larrick

INTRODUCTION

N Reactor pressure tube 1756 (HT 626) and its associated nozzles were removed from the N Reactor in May 1966 for postirradiation examination in accordance with planned surveillance procedures. This tube was original equipment and had been in-reactor since startup. Total exposure in-reactor was approximately 300 operational days. Operational temperatures were 360°F at the inlet and 512 ± 7°F at the outlet. Prior to installation in-reactor, the tube had been etched and then autoclaved 72 hours in 425°C, 20 psi steam. A complete description of the fabrication history is given elsewhere.(1) The postirradiation examination was divided into two parts: first, mechanical tests, which included visual, ultimate strength burst, brittle fracture, tensile, microhardness and metallographic tests; and secondly, corrosion tests which included visual observations, absorbed hydrogen analyses, and oxide thickness measurements on the pressure tube and an evaluation of pitting on the nozzles. The mechanical properties evaluation has been reported by Evans and Aungst(2) and this report presents the corrosion evaluation.

SUMMARY AND CONCLUSIONS

N Reactor Zircaloy-2 pressure tube No. 1756 and its associated ASTM A234 steel nozzles were examined for corrosion and hydrogen content after approximately 300 days exposure in-reactor. Visual examination showed tight, adherent, dull black oxides in the pressure tube except for scratching in the bottom due to sliding of fuel and fuel spacers through the tube during charge-discharge operations. Several fretted areas up to 3/8 inch wide by 1/2 inch long by up to 13 mils deep were observed at the downstream end--these pits were caused by vibration of the fuel spacers against the pressure tube.

Hydrogen levels were fairly constant along the tube length with an average of about 19 ± 6 ppm except at one location. At approximately 30 inches from the front end of the tube a sharp peak to a maximum of 58 ppm hydrogen occurred. The reason for the peak is unknown.

Measurements of oxide thickness were made on the OD and ID of the pressure tube at several locations along the length of the tube. Oxide thickness, as converted into weight gains, on the surfaces exposed to the reactor gas environment (OD) remained fairly constant in the range of 32 to 46 mg/dm^2 along the entire tube length except at the rolled joints at the very ends where it was higher. An archive piece of OD surface removed from the rear end of the tube before installation in the reactor had a weight gain of 42 to 47 mg/dm^2. Weight gains on the surfaces exposed to the ammoniated water coolant (ID) were 37 to 50 mg/dm^2 at the rolled joint (water inlet) and linearly increased along the tube from 31 to 45 mg/dm^2 near the front rolled joint to 59 to 66 mg/dm^2 at the rear end. Weight gains on the ID surface of the archive piece and correspondingly on the tube, are about twice as high as expected from out-of-reactor data but do not show any definite effect of reactor flux.

Numerous shallow pits and a few larger pits up to 0.026 inches deep were found in the low alloy steel nozzles; however, visual and metallographic examinations showed that the oxides in the pitted areas were similar to those in the nonpitted areas, indicating that the pitting which occurred during prestartup testing was no longer active. The existing pits were no more susceptible to new corrosion than nonpitted areas when exposed to semitreated water.

RESULTS

General Observations

The pressure tube was cut into several pieces at N Reactor. The more radioactive pieces were sent to the Radiometallurgy Laboratory and the less radioactive pieces were examined in the Corrosion Laboratory. A diagram showing where the various test samples were removed from the pressure tube is shown in Figure 1.

Visual observations were made on the end sections of the pressure tube where low radiation levels permitted examination. Numerous scratches due to sliding fuel and fuel spacers along the tube were seen in the bottom third of the tube circumference. Figures 2 and 3 show 2X and 10X photographs of the scratches. The scratches were shallow (<0.5 mils) and did not significantly change the tube thickness. Localized, accelerated corrosion did not appear to be occurring at the scratches as determined by the lack of any thick white oxides. Most of the scratches had a shiny metallic color while a few had a gray-brown oxide forming over the surface. Some galling of the process tube was observed but no inclusions of material rubbed off the fuel or spacers was noticed. It has been postulated that small slivers of the galled pressure tube is the source of the Zircaloy-2 which has been found lodged against fuel elements and has caused fuel cladding failure due to a fluttering action in the coolant, resulting in fretting corrosion.(21)

The oxides at the non-scratched areas appeared to be smooth, tightly adherent and dull dark gray to dull black in color, along the entire length of the tube. Scratches were not observed in the top two-thirds of the tube.

Large oval pits about 3/8-inch wide by 1/2-inch long were found in the downstream end of the tube at each location corresponding to where a spacer support foot contacted the bottom of the tube. No pits were seen at locations where fuel support feet contacted the tube, but some of these areas were burnished. Typical pits formed by spacer feet are shown in Figure 4. Additional pits are shown in Photograph 4, Reference 2. The pits shown in Figure 4 were formed by the feet on spacers next to the fuel at locations corresponding to tube sections 3 and 4 in the sectioning diagram (Figure 1). These marks were much deeper than the marks caused by the spacers farther downstream in the tube. Pit depths were approximately 13 and 10 mils deep for tube sections 3 and 4, respectively. The apparent cause was fretting due to vibration of the spacers. Metallographic sections through the fretted areas are shown in Figures 5 and 6. Figure 5a shows an 8X macro and 5b and 5c show typical areas inside the fretted area at location No. 3. The dark second phase precipitates in Figures 5b and 5c are unidentified material but are not hydrides. Additional photographs showing second phase precipitates for this tube are shown in Reference 2 and photographs of precipitates for other tubes are shown in Reference 3. Figure 6a shows an 8X macro and Figures 6b and 6c are photomicrographs showing typical areas inside the fretted area at location No. 4. Evans and Aungst reported pit depths as deep as 10 mils on replicas of areas 3 and 4 made before the tube was cut for metallography.(2)

Hydrogen Analyses

Hydrogen analyses were conducted by hot vacuum extraction of samples taken at several intervals along the length of the Zircaloy-2 pressure tube. The more radioactive center sections were analyzed in the Radiometallurgy Laboratory and the less radioactive end sections were analyzed in the Analytical Laboratory. The results are shown in Figure 7. Except for one location, the hydrogen content was nearly uniform along the tube length. Hydrogen levels for most of the tube length, including the areas exposed to the maximum neutron flux, ranged from 15 to 26 ppm with an average of about 19 ppm. This compares to a hydrogen content of 15 ppm on an archive sample cut from the tube before reactor operation. The exception was a very pronounced peak which occurred at approximately 30 inches from the front of the tube. Hydrogen levels up to a maximum of 58 ppm were observed at this location. Numerous samples at closely spaced intervals on either side of the peak confirmed that a peak definitely existed at this location but did not provide any evidence on why the peak occurred. An enlarged view of Figure 7 at the area near the hydrogen peak is shown in Figure 8. Samples for hydrogen analyses were taken at three locations circumferentially around the pressure tube; Figures 8b and 8c show the analyses at two locations 90 degrees apart in the scratched area at the bottom of the tube and Figure 8a shows the analyses 180 degrees from one of the scratched areas at a location near the top of the pressure tube where scratching did not occur. The scratching in the pressure tube was caused by charge-discharge operations involving the reactor fuel and spacers. The hydrogen peak occurred at all three locations and was of similar magnitude indicating circumferential distribution was fairly uniform.

Metallographic analyses made at 30 inches from the front rolled joint (area of peak hydrogen) showed the hydrogen to be precipitated in the inside half of the wall thickness, although not in the form of a case. Metallographic examination for precipitated hydride in the longitudinal direction through the peak area failed to show the peak obtained by vacuum extraction analyses.

Metallographic sections through three fretted areas (two are shown in Figures 5 and 6) did not reveal any accelerated hydriding occurring in these areas nor any radial distribution of hydrides as occurred at the 30-inch location.

A complete longitudinal metallographic traverse for hydriding was made on the three-inch long front and rear rolled joint sections of the pressure tube. One small area containing three patches of hydride needles was found on the upstream tip of the upstream rolled joint; no other patches of hydriding were found. The largest of the three hydride patches is shown in Figure 9.

Oxide Measurements

Measurements of oxide thickness were made at several locations along the pressure tube length by mounting a metallographic sample in mounting compound and carefully polishing perpendicular to the tube surface. Oxide thicknesses were measured through a microscope with a calibrated Filar eyepiece and these thicknesses were converted to mg/dm^2 weight gain by multiplying by the theoretical density of ZrO_2 and a correction factor consisting of the weight ratio of O_2 to ZrO_2. The results are shown in Figures 10 and 11. Figure 10 shows the weight gains observed on the tubing ID surfaces which were exposed to the water coolant and Figure 11 shows the weight gains observed on the tubing OD surfaces which were exposed to the reactor gas atmosphere. Each point on the curve is an average of five to ten measurements taken at arbitrary intervals along a small segment of the sample.

The calculated weight gains on the ID surface were 37 to 50 mg/dm^2 at the inlet (rolled joint), and linearly increased along the tube from 31 to 45 mg/dm^2 near the front rolled joint to a value of 59 to 66 mg/dm^2 at the outlet. The values at the outlet were somewhat higher than the 41 to 52 mg/dm^2 measured on an archive piece cut from the downstream end of the tube after autoclaving but before installation in the reactor, indicating 10 to 20 mg/dm^2 corrosion occurred during the exposure period.

Except for at the ends of the pressure tube at the rolled joint areas, the weight gains on the OD surface along the length of the tube were fairly constant at about 32 to 46 mg/dm^2. At the ends of the tube (rolled joint) the weight gains were somewhat higher than along the rest of the tube. The magnitude of the weight gains over most of the tube was similar or lower than those measured on the archive sample, indicating little, if any, corrosion occurred on the OD during the reactor exposure period.

Typical oxide films on the tubing OD and ID are shown in Figure 12. Position numbers refer to the sampling diagram in Figure 1. Photographs of the oxides at scratched areas showed areas lacking oxide and other areas where new oxides were forming.

Nozzle Examination

Both front and rear nozzles were cut into 11- to 14-inch long sections and each section was then split longitudinally for examination. Photographs of the split nozzles are shown in Figure 13. Each section is labeled in Figure 13 for identification in subsequent figures. The inside diameters of both nozzles were covered with thousands of broad, shallow pits 1 to 2 mils deep. In many cases these pits had joined to form long shallow lines of attacked area. They tended to be oriented in the direction of metal flow from fabrication. Several more severe pits were also found, mostly associated with areas where fuel spacer feet had been in contact with the nozzles. Figures 14 through 16 show closeup views of the nozzle sections and magnified views of a few of the more severely corroded areas. Measurements on cross sections through the three deepest pits, shown in Figure 17, gave pit sizes of 0.02 in. deep by 0.06 in. wide for one pit; 0.026 in. deep by 0.145 in. wide for another pit, and 0.002 in. deep by 0.0675 in. wide for the third pit. Most of the pitting is attributed to exposure to oxygenated, filtered water which was passed through the reactor for about a six week period before reactor startup. This water is typically quite corrosive to steel.

Both nozzles had tightly adherent, dull-black, uniformly-thick oxides. The oxides in the pitted areas looked very similar to the oxides at the non-corroded area; indicating that the pitting corrosion which occurred during exposure to semitreated water before startup was no longer active.

There was not any buildup of corrosion products in any of the pits other than the thin black oxides. Metallographic sections through the pitted areas and non-pitted areas, as shown in Figure 18, indicate that the oxides are continuous, tightly adherent and similar at both areas. Large, tubercular corrosion product formations or no oxides at all are the two most common surfaces found on active pits. Oxide thicknesses on the inlet nozzle were thinner (0.03 to 0.07 mils) than on the outlet nozzle (0.03 to 0.16 mils); probably because of the lower temperature at the inlet nozzle.

The steel surfaces of the nozzle in contact with the Zircaloy-2 in the rolled joints had shiny interference films indicating very little corrosion. The films were slightly darker on the rolled joint on the downstream nozzle than on the upstream nozzle. A continuous circumferential line of pits in both nozzles was found at the crevice area where the end of the Zr-2 butted against the nozzle. The pitting appeared to be slightly worse on the front rolled joint junction than on the rear rolled joint junction. A typical area of pitting is shown in Figure 19; maximum pit diameter was about 30 mils. There were no indications of leakage past the grooves in the rolled joint but the center groove on the rear rolled joint was rusty colored, indicating that moisture had been present. The lack of rusting on the grooves on either side of the center groove indicates that the moisture came through the weep hole drain collection system. Whether or not the source of the moisture in the drain system was from leakage of another tube connected to the system or some other source is unknown.

Emission spectrochemical analyses and X-ray diffraction analyses were conducted on a composite of oxides scraped from the bottoms of several pits. None of the X-ray diffraction lines matched to any degree of accuracy with ASTM patterns; therefore, the crystalline compound(s) present is unknown. The results of the emission spectrochemical analyses and the composition of the A234 steel base material are given in Table I. The major constituent of the oxides was iron; because of this, the fact that the oxides were uniform, tight and black, and the fact that the major corrosive media was high-temperature water, it is assumed that the oxides in the pits and on the nonpitted internal nozzle surfaces were magnetite.

TABLE I

EMISSION SPECTROCHEMICAL ANALYSES OF OXIDES IN PITS

Element	Concentration Wt. Percent ±Factor 2	Normal Concentration In Base Metal** Wt. Percent
Ag	-	
Al	0.2	
As	-	
B	-	
Be	-	
Bi	-	
C	*	0.1 to 0.20
Ca	*	
Cd	-	
Co	0.5	
Cr	*	1.00 to 1.50
Cu	0.05	
Fe	>50.	balance
In	-	
Ir	-	
Mg	0.1	
Mn	0.1	0.30 to 0.80
Mo	-	0.44 to 0.65
Ni	0.01	
P	-	0.04 maximum
Pb	0.01	
Pt	-	
S	-	0.040 maximum
Si	2.	0.50 to 1.00
Sn	-	
Ti	-	
V	-	
Zn	0.5	

\- None detected

* Interference

** Base metal is ASTM A234, Gr WP-11 steel. Concentrations given are nominal ASTM specifications and not direct analyses.

Two samples approximately 2 in. long by 1 in. wide were cut from the outlet nozzle and exposed to flowing (>5 gal/min) filtered Columbia River water. The object of the test was to determine if the existing pits in the nozzle would selectively reactivate if the nozzle was re-exposed to a corrosive coolant. Should reactivation occur, repeated exposures to semitreated water (filtered but not deionized) would cause much more rapid penetration of nozzles, pipe walls, etc. than if new pitting sites were initiated. The results, given in Table II, indicate that the old pitting sites will not preferentially corrode in filtered Columbia River water.

DISCUSSION

Oxide Measurements on Zircaloy Pressure Tube

The weight gains on the archive samples cut from the reactor pressure tube before installation in the reactor were much higher than would be expected from the standard published corrosion curves. The pressure tube was autoclaved 72 hours in 20 psi steam at 425°C (800°F). Standard corrosion curves (Figure 20; 800°F, 1500 psi steam) indicate a weight gain of about 29 mg/dm^2 should have been obtained in 72 hours compared to the 41 to 52 mg/dm^2 actually obtained. Weight gains obtained on corrosion coupons exposed along the length of the pressure tubing during the autoclaving are shown in Figure 21 and are in much better agreement with the standard curves (slightly lower). An uncertainty is introduced in that the standard curves were obtained at 1500 psi and the autoclaving was conducted at 20 psi.

In order to resolve some of the discrepancies concerning the higher than predicted autoclave weight gains on the pressure tube, the 1-inch long section of tube shown in Figure 1 between sections 12 and 13 was re-etched and autoclaved 72 hours in 20 psi, 425°C steam. The weight gain as measured from weight change on the sample was 20.9 mg/dm^2.

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TABLE II

Corrosion of Nozzle Samples in Flowing Filtered Columbia River Water

Exposure Period, Days	Description
0.33	Fresh saw-cut metal surfaces on edges of samples have thin coating of orange rust. A few flecks of rust were forming at random locations on black magnetite covered surfaces. One pit where oxide had been scraped out was rusting. All other pits and remaining unpitted surface were still black.
1.3	Slightly more rust at same locations as described above.
7	Rust build-up slightly increased. One pit had 4 or 5 small dots of rust around its rim but none in the bottom of the pit. Numerous pinpoint tubercules are forming on the magnetite surface at areas where the rust flecks above were observed.
26	Bare (saw-cut) metal surfaces now have ∿1/64-inch thick orange oxide and numerous 1/16-inch high tubercules. Numerous 1/32-inch high tubercules scattered on oxided surface with black original oxides in between. Several original pits are still black.
47	Started adding sulfite oxygen scavenger to water. Similar to above, tubercules slightly larger.

A coupon from the same lot of material that was used for control coupons during the original autoclaving (Figure 21) was also autoclaved; it had a weight gain of 17.0 mg/dm^2. These weight gains were much lower than predicted by the published curves (Figure 20). The visual appearance of the oxide on the tube sample after this second autoclaving was much different than the oxide present from the original autoclaving. The original oxide appeared to be uniform, thick and dull black while the second oxide was uniform, thinner, and shiny black.

The tubing from the second autoclaving was metallographically sectioned and the film thickness was measured in the same manner as was the film thickness on the pressure tube after it was removed from the reactor. Weight gains, calculated as before from film thicknesses, were 20.7 mg/dm^2 on the OD and 25.0 mg/dm^2 on the ID. Since these thickness measurements closely match the weighing measurements, this technique of obtaining weight gains appears to be valid and thus the high weight gains measured on the pressure tube are valid. Similar agreement between weighing and thickness measurements was found on a coupon with 58 mg/dm^2 oxide.

The weight gains obtained during the second autoclaving of the above 1-inch tube sample were somewhat lower than the standard weight gain curves and thus indicate that the pressure tube Zr-2 is basically good, corrosion-resistent material. Therefore, there is another, unknown reason for the cause of the high measured weight gains on the pressure tube. It was probably due to the surface condition of the tubing rather than a condition existing in the autoclave since weight gains of the coupons autoclaved with the pressure tube shown in Figure 21 appear to be normal. If the tubes were inadvertently autoclaved for a longer period of time, such as a double autoclave cycle, it would have shown upon the coupon weight gains and since no such effect was observed, this possibility must be ruled out. Whatever the reason for the higher autoclave weight gains, it affected the weight gains on many tubes other than the one examined. Weight gains on archive samples from six other tubes, as measured by oxide thickness, ranged from 41 to 56 mg/dm^2 which is similar to that on the archive sample from the pressure tube examined in the report.

Residual fluoride ion from the etching could have been associated with the high weight gains but is not too likely as residual fluorides usually cause a slightly milky colored oxide and none was observed on the tubing after autoclaving or after removal from the reactor. It is possible that not enough metal was removed during the etching process and residual contaminants from tube fabrication remained in the surface layers. If this were true, the contaminants were in very small amounts as the second etching and autoclaving resulted in standard weight gains.

Allen et al.,(5) have shown that minor variations in autoclave proof tests can cause significant variations in weight gains on Zr-2. For example, they found that weight gains were 2 to 4 mg/dm^2 higher in 72 hour, 1500 psi, 400°C autoclaving if the samples were initially in water than if they were in steam during autoclave startup. The effect was less noticeable in 100 psi, 400°C autoclaves; conditions approaching the 20 psi autoclaving to which the N-Reactor pressure tube was subjected. They attribute the lower weight gains to more exposure to molecular oxygen. Allen(5) also found that pressure affects some batches of Zr-2 much more than other batches. He defines various batches as "good" or "bad"; the "bad" material is defined as material which exhibits higher short term corrosion rates following proof testing at 100 psi than at 1500 psi. The material in the example above concerning wet or dry startup was "good" material. The weight gain of "good" material was affected by water or steam startups but very little by pressure. The weight gain of "bad" material was little affected by type of startup but was very significantly affected by pressure--the weight gain for "bad" Zr-2 was 10 to 20 mg/dm^2 greater in 100 psi proof tests than 1500 psi proof tests. At 1500 psi, the "bad" material met accepted weight gain standards. The appearance of the "bad" materials after proof testing at 100 psi was not so black and glossy as with normal materials. The most clear-cut distinction between "bad" and "good" material to explain why they exhibited different corrosion characteristics was the distribution of intermetallic precipitates from the Fe, Cr, and Ni alloying constituents. "Bad" materials all had areas 10 microns or more which were devoid of intermetallic precipitates; they also had much larger precipitates than "good" material. Annealing the "bad" material at 750°C precipitated many fine intermetallics and this material then behaved similar to "good" material. Beta-quenching gave an intermediate intermetallic precipitate distribution and autoclaving proof tests at 100 psi gave normal, low weight gains but subsequent corrosion weight gains were very high.

The behavior of the materials Allen classified as "bad" closely resembles the behavior of N-Reactor pressure tube material archive samples--both had much higher than normal proof-test weight gains and both had dull black oxides. The N-Reactor tube was autoclaved at a low pressure (20 psi) and it was at low pressures that the "bad" characteristice showed up in Allen's tests. Many large intermetallic precipitates were noticed in the N-Reactor pressure tubing (Figures 5c, 6c) which resembled those found by Allen. However, the presence of widely dispersed intermetallics does not explain why low weight gains were found when the section of N-Reactor pressure tubing was re-etched and reautoclaved. This treatment should not have affected in any way the intermetallic precipitates.

The data from the coupons installed in the autoclave at the time the pressure tube was autoclaved show lower weight gains at 100 inches from the front of the autoclave than did the other coupons at other locations (Figure 21). The temperature variation (Figure 21) was not large enough to account for these lower weight gains and the pressure tube OD weight gains do not bear out the dip in this location. (The upstream end of the pressure tube corresponds to the front of the autoclave.) Since these coupons correspond to "good" material under Allen's definition, it is possible that localized wet or dry conditions could have existed along the autoclave and caused the variations.

The calcualted weight gains on the ID surfaces of the downstream end of the Zircaloy-2 pressure tube after removal from the reactor were much higher than predicted by out-of-reactor data. Data in the literature and shown in Figure 20 indicate that a freshly etched Zircaloy-2 surface in the alpha condition will exhibit a straight-line corrosion curve when log weight-gain is plotted against log-time.(4) Unpublished data obtained in this laboratory indicate that if Zr-2 samples are exposed at one temperature and transferred to another system at another temperature (these experiments were conducted at 300 to 400°C) the sample will immediately start corroding at a rate in the second system corresponding to that of a sample that had always been in the second system and corroded to an equivalent weight gain. This is true for pretransition oxides but not for post transition oxides. There appears to be a memory effect for post transition oxides. Thus, for the case of an N-Reactor tube which had been autoclaved to 40 mg/dm^2 before installing in the reactor and then exposed in water for 300 days at 500°F, the starting point for the reactor corrosion period would be the point in Figure 20 on the 500°F curve corresponding to 40 mg/dm^2. Three hundred days additional exposure from this point on the 500°F curve corresponds to 41 mg/dm^2 or an additional 1 mg/dm^2 corrosion. Because of the log-log nature of the curves, preautoclave weight gains much less than 40 mg/dm^2, say 10 mg/dm^2, would result in slightly higher in-reactor gains--about 4 mg/dm^2 for example. These examples of expected corrosion are much less than actually observed. The actual weight gains observed on the ID surfaces at the downstream end of the pressure tube (59-66 mg/dm^2) over those observed on the archive tube (41-52 mg/dm^2) were much higher than expected. Since the pre-exposure autoclave weight gains were close to the transition weight gain there could have been a partial memory effect which carried over to the reactor exposure period. If so, this memory effect was in operation only at the higher-temperature, downstream-end of the pressure tube. The weight gain versus tube length curve shown in Figure 10 reveals that the weight gains on the ID surface of the upstream end were slightly less that those on the archive sample. Oxide dissolution into the base metal is thought not to be a factor because of the low temperatures involved.

It was stated above that the ID downstream weight gains could have been affected by a partial memory effect. Consider the case where the autoclave weight gains had been beyond the transition point where breakaway corrosion occurs; it then would be expected that a total memory effect would have been in operation and that the corrosion in-reactor would have continued just as if the tube was still in 800°F (425°C) steam. Three hundred days exposure at this condition would have resulted in a weight gain of about 400 mg/dm^2, much higher than the 59 to 66 mg/dm^2 actually found. Thus, if a memory effect is the cause of the high downstream weight gains, it is only a partial memory effect.

The example given for the above illustration was an autoclave weight gain of 40 mg/dm^2. The archive sample weight gains calculated from film thicknesses actually ranged from 40 to 52 mg/dm^2. Forty mg/dm^2 on the standard curve is less the breakaway transition point in 800°F steam, but 52 mg/dm^2 is above it. Because of the scatter in the archive data and because of inherent uncertainties in the standard curve, the exact condition of the tube (pre- or post-breakaway) after autoclaving is quite nebulous.

There is also the possibility that the downstream end was more corrosion prone than the upstream end. The weight gains on the archive sample (40 to 52 mg/dm^2, downstream end) were higher than the post-reactor exposure weight gains on the upstream end of the pressure tube (31-45 mg/dm^2). With the same corrosion resistance at each end, it would seem these weight gains should have been similar. Some lots of Zr-2 are more corrosion prone than other lots and it is possible that one end of a long tube could have different corrosion characteristics than the other end. This does not appear to be due to chance, however, since the weight gains on archive samples from six other tubes were similar to the archive gains on the tube examined. The six other high archive weight gains suggest something common to all the tubes somewhere in their fabrication history which caused the high autoclave weight gains.

The weight gains on the OD along the entire length (except at the downstream end of the tube and in the rolled joints) were comparable to the weight gains on the upstream end of the ID. At the downstream end and on the archive sample the OD weight gains were slightly higher and were comparable to the ID archive weight gains. Since the OD weight gains were lower (and constant) along most of the tube length than on the archive sample, it appears that little OD corrosion occurred in-reactor. This does not agree with data reported by Shannon and Hope, where weight gains of 22 to 26 mg/dm^2 at 290°C, 41 to 55 mg/dm^2 at 350°C, and 167 to 176 mg/dm^2 at 400°C were obtained in 4000 hour, in-reactor capsule tests in gas atmospheres simulating N-Reactor atmosphere.(17) Out-of-reactor control samples produced weight gains of 0.9 to 1.2 mg/dm^2 at 290°C, 8.7 to 10.7 mg/dm^2 at 350°C and 52.8 to 68.0 mg/dm^2 at 400°C in Shannon's tests.(17) All samples were Zr-2 preautoclaved 72 hours in 400°C, 1500 psi steam, conditions similar to N Reactor pressure tube preautoclaving (72 hours, 425°C, 20 psi steam). Later data,(15) did not duplicate the accelerated in-reactor corrosion, so for purposes of comparing with the N Reactor tube weight gains the out-of-reactor values above can be used. A large uncertainty in making a comparison is determining what the actual tube OD temperature is. The maximum calculated OD tube temperature predicted for an N Reactor tube is 368°C;(15) this value should be used as an upper limit and it is not expected that the OD temperature of Tube 1756 came anywhere near this temperature. If the tube OD temperatures were in the neighborhood of 290°C, the predicted in-reactor weight gain of about 1 mg/dm^2 would not be detectable in the scatter of OD weight gains actually found. Some OD oxidation had to occur in order to prevent gas-side hydrogen absorption as discussed later.

The effect of neutron flux on oxide weight gains on the N Reactor pressure tube in uncertain. Evans and Aungst estimated from mechanical strength considerations that the maximum exposure of the tube to neutrons (greater than 1 MeV) was 3 to 4 x 10^{20} nvt.(2) Calculations indicate the maximum flux >1 MeV was 1.2 x 10^{21} nvt.(6) Johnson has reported in-reactor weight gains of 11 and 52 mg/dm^2, respectively, on Zr-2 preautoclaved in 400°C, 1500 psi steam and then exposed to pH-10, 280°C (536°F) ammoniated water at fast flux exposures of 2.1×10^{20} nvt and 7.8×10^{20} nvt.(7) A gain of 50 mg/dm^2 in the N Reactor tube would certainly have been seen on the weight gain versus length graphs but a weight gain of 10 mg/dm^2 easily could be hidden in the data scatter. Any large effect of flux would probably have caused an increase in gains at the center of the reactor where the flux was at a maximum and resulted in a hump in the curve rather than the straight line actually observed. Such a hump has been seen on curves of weight gain on pressure tubes removed from the Plutonium Recycle Test Reactor (PRTR).(8)

Factors which could reduce an effect of flux on corrosion rates are the reduced oxygen and temperature levels as compared to Johnson's tests. Oxygen has been shown to definitely increase Zr-2 corrosion in-reactor and the N Reactor pressure tube was exposed to water containing very low oxygen levels. Samples of other N Reactor tubing exposed in the ETR in oxygenated, lithiated water for a comparable time (300 days) but higher flux (3×10^{21} nvt) had weight gains of 600 mg/dm^2. The difference in temperature between the two tests may not be significant. Normally lower temperatures result in lower corrosion rates but the N Reactor pressure tube was exposed at temperatures only slightly less than those to which Johnson exposed his samples (see page 1); whether or not it was sufficiently lower to mask an effect of flux is unknown. The above referenced effect of flux on weight gain in the PRTR was at temperatures comparable to those in N Reactor which also indicates that the temperature may not be a significant factor.

The reason for the increase in oxide thickness at the rolled joint at each end of the tube is unknown but could have been caused by damage of the autoclave oxides or work hardening during the rolling operation, or possibly by contact with the steel nozzles.

Hydrogen Analyses

One of the major concerns before the pressure tube was removed from the reactor was whether or not gas side (OD) hydriding would occur.

Shannon found that extensive hydriding occurred in Zr-2 in a nonoxidizing helium-hydrogen-carbon monoxide gas mixture at temperatures similar to those expected on the gas side of the N Reactor pressure tube.(12) This was true for both etched and autoclaved samples; the autoclave film initially prevented hydriding but it broke down with time and then hydriding proceeded. If sufficient amount of an oxidant such as water vapor was present the hydrogen absorption reaction was stifled due to the continuous formation of an oxide film. This was shown in later mechanism studies when it was found that hydriding of the Zircaloy occurred when the water supply rate became diffusion limited to the extent that water molecules no longer reached the surface as fast as they would normally be consumed in the oxidation reaction.(13,14) This meant that when sufficient water vapor was available, the zirconium oxidation rate was independent of the actual partial pressure of water (at a given temperature), and hydriding was inhibited. Additional work showed that the minimum required water vapor was 0.13 mm H_2O (dewpoint of -35°F) in the reactor inlet gas.(15,16) The minimum water requirement was based on worst case temperature assumptions, diffusion of the water from the gas through the graphite to the pressure tube, etc. For a more complete analyses the reader is referred to the referenced literature. It should be mentioned that even though a minimum amount of water is required in the reactor gas to continuously oxidize the pressure tube, too much water aggressively attacks the graphite stack and leads to rapid graphite burnout. An upper water vapor level of 0.53 mm (-11°F dewpoint) was established; at this concentration 2% burnout in 1000 days will occur at the maximum expected graphite temperature of 820°C.

The oxidation rate on N Reactor Pressure Tube 1756 on the gas side (OD) apparently was high enough to stifle hydrogen absorption from the gas as determined by the following calculation.

First, to get an idea of how much hydrogen was in the tube before in-reactor installation, consider a one-foot length of pressure tube and a weight gain during autoclaving of 40 mg/dm^2 on both OD and ID. A total of 64 mg hydrogen would be formed during the autoclaving corrosion reaction. Assuming 50% of this hydrogen is absorbed into the metal

(2990 gm in one foot length) the resultant hydrogen increase in 11 ppm. When added to the 14 ppm hydrogen analyzed to be in the pressure tube by the manufacturer before autoclaving, a total of 25 ppm hydrogen is indicated to be in the pressure tube before installation in-reactor. Since the measured hydrogen levels over most of the tube length were 19 ± 6 ppm, or slightly less than the calculated pre-installation level, it seems that the hydrogen levels measured after tube removal are accounted for by pre-installation hydrogen and are not due to gas phase hydriding.

The hydrogen levels formed by autoclaving obtained by the above calculations are dependent on two nonexact assumptions which affect the magnitude of the calculated hydrogen content. The 40 mg/dm^2 weight gain chosen was about half-way between the 30 to 50 mg/dm^2 range found over most of the tube length. For this particular surface area to volume ratio on this pressure tube and a 50% absorption efficiency, about 1 ppm hydrogen is absorbed for every 4 mg/dm^2 weight gain. Thus, the actual calculated error from assuming an incorrect weight gain is ± 2.5 ppm hydrogen over the 30 to 50 mg/dm^2 weight gain range. The 50% absorption efficiency figure was chosen on the high side of the expected amount of absorption. Absorption efficiency has been found to range from 10 to 100% but typical values are normally about 20 to 30%. If 25% absorption efficiency is used, the autoclave induced hydrogen is closer to 6 ppm, for a total pre-installation hydrogen content of about 20 ppm. This does not change the above conclusion that significant gas phase hydriding did not occur in-reactor.

The 15 ppm hydrogen content on the archive sample (autoclaved) at a first look indicates little hydrogen pickup occurred during autoclaving, but it should be remembered that this is only one analysis and falls within the 19 ± 6 ppm range found on the in-reactor tube.

Some comments on the high hydrogen levels found 30 inches from the upstream end of the pressure tube are warranted by the above calculations. In order to get the hydrogen by a normal corrosion mechanism it would necessary that 58 minus 14 or 44 ppm hydrogen be absorbed during th corrosion process. This is equivalent to a required weight gain of over 160 mg/dm^2 where a weight gain of less than 40 mg/dm^2 actually was found at this area, indicating some other source of hydrogen. At this time there is no way of knowing whether or not the high hydrogen levels at the thirty inch location were in the pressure tube before installation in-reactor or if they were caused by an in-reactor absorption process. Additional tube examinations should clear up this point.

The upstream end of the pressure tube and its associated thimble surrounding the tube OD projects 54 inches into the air from the edge of the reactor (shield plate) and all but about the end 10 inches of the tube is exposed on the OD to the reactor gas system in the crevice formed between the pressure tube and the thimble. Since there is essentially no gas recirculation in the crevice area, it would be expected that very little heat transfer would occur and the pressure tube would be essentially at the same temperature on the OD as at the ID. (If heat transfer did occur, it would be expected that heat would flow from the pressure tube, through the gas space, through the thimble and to the air.) Both the ID and OD temperature would be approximately the reactor inlet water temperature, or about 360°F. Without a radial thermal gradient on the pressure tube any hydrogen absorbed would be expected to remain near the point of absorption. With a thermal gradient the hydride tends to migrate to the cooler surface which in this case would be the OD surface, however, the hydride was observed nearer the ID surface.

The radial distribution of the hydrogen in the pressure tube is very important in determining the hydriding mechanism. A difference in radial distribution would provide a clue as to whether or not the source of the hydrogen was from the ID or OD surfaces. A microscopic examination of the metallographic samples taken at the hydrogen peak showed that most of the hydride needles were located near the ID surface but not in the form of a case, which suggests that if the hydrogen absorption occurred during the in-reactor exposure it initiated from the ID surface. These needles were very small and it was necessary to use a 600X magnification in order to see them rather than a 250X magnification which is normally used

It is difficult to determine from metallography alone whether or not the gradient observed represents the true radial hydride profile. It is possible that the radial hydrogen distribution was uniform from ID to OD but that visible precipitates formed only near the ID surface. In this case it would be necessary to remove successive layers of the pressure tube and analyze these by hot vacuum extraction to determine the true distribution. Such a method of analyses is suggested for future pressure tube examinations.

No real explanation for the cause of the peak in the hydrogen concentration curve is available but the peak does roughly correspond to the upstream end of the internal spacer loading charge.

A normal loading for process tube No. 1756 during the period when it was in the reactor starting at the downstream end consisted of four 27-1/2 inch long carbon steel spacers, two 15-1/2 inch carbon steel spacers, a fuel charge approximately 417 inches long, two 15-1/2 inch spacers and three 27-1/2 inch spacers. Approximately 23 inches of empty space is found to exist at the upstream end of the Zr-2 tube, assuming the tube is 53'-3" long. The location of the upstream-most spacer thus roughly corresponds to the location of the peak hydrogen content shown in Figure 4, whether there is any real connection is unknown.

One possible mechanism associated with the spacers that could have caused the excessive hydrogen concentration at the 30 inch location is a galvanic coupling between the fuel spacer column and the pressure tube. For this to occur, the pressure tube would have to be cathodic to the spacers. Since the upstream spacer column terminates near the 30-inch location this would be a logical location for any currents available to discharge. Such a galvanic mechanism occurs in the downstream end of Hanford K Reactor pressure tubes, but in this case the fuel and fuel spacers are aluminum alloys in a Zircaloy-2 pressure tube. The temperature and water quality are also considerably different in the K Reactors than in the N Reactor. The aluminum and Zircaloy-2 in the K Reactors are widely separated on the galvanic series scale and this metal combination would be expected to induce a galvanic cell but the carbon steel and Zircaloy-2 in the N Reactor are close on the galvanic series scale so that a galvanic cell would not be expected. If a potential did exist and the Zr-2 pressure tube was the cathode of the couple, an electrochemical hydrogen charging mechanism could be postulated. In-reactor potential measurements would be desirable if tubes removed in the future also have high localized hydrogen concentrations.

Some evidence that the hydrogen peak may be caused by an electrolytic process can be inferred from out-of-reactor tests conducted by Winegardner.(11) When he electrolytically induced hydrogen in Zr-2, the needles were very small and it was necessary to use higher magnification (600X) than normally used (250X) to see precipitated hydrides in metallographic samples. The small needles he electrolytically induced were similar in size to those found in the N Reactor pressure tube at the hydrogen peak area.

Another possible source of hydrogen is from the water coolant. Radiolytic decomposition of the water into hydrogen and oxygen and of the ammonia (used to control the pH of the coolant) into hydrogen and nitrogen occurs in the flux zone. The hydrogen would be in the form of dissolved molecular hydrogen at the upstream area where the high zirconium hydride concentration was found but would be in both atomic and molecular forms in the flux zone. At the normal N Reactor coolant hydrogen concentrations of 40-60 cc/l, very little, if any, hydrogen absorption would be expected(21) but at very high hydrogen concentrations (∿15700 cc/l) considerable hydrogen pickup by the zirconium would be expected.(22) There is a small possibility that at the N Reactor dissolved hydrogen concentrations that absorption could occur if the oxides were removed due to constant wear caused by a constant slight motion of the upstream spacer foot against the pressure tube and the oxidizing power of the water coolant was not sufficient to continuously reform a new oxide.

The cause of the three small patches of hydride found in the rolled joint area (Figure 9) cannot be clearly explained and is another item which should be more thoroughly investigated during future tube examination. Possible explanations are (1) the hydride platelets were present before installation, (2) mechanical damage during rolling of the tube into the nozzle allowed corrosion hydrogen to enter at this point, or (3) the hydriding is somehow associated with the contact with the steel nozzle. Small, localized patches of hydride platelets were found by Larrick in Zircaloy-2 samples in contact with carbon steel in the N Reactor Graphite Cooling System.(10) These Zr-2 samples were rods screwed into threads on a carbon steel cap so that most of the sample protruded into the water coolant stream. The hydride platelets were found on the threads furthest from the water and deepest into the steel cap.

Fretting Corrosion

Fretting corrosion similar to that found in Tube 1756 has also been found in other pressure tubes in N Reactor.(18,20) Sixteen tubes were examined with a TV boroscope in May, 1966 and fretting marks were found at the downstream end of the pressure tube at the locations where downstream spacer feet (supports) contacted the tubes. Front spacer feet locations were barely discernible and fuel element support locations were readily discernible but no penetration of the ZrO_2 occurred at these two areas. Out-of-reactor tests showed that chattering occurred on downstream spacers under typical flow conditions, indicating that fretting, and not a galvanic corrosion attack, is the cause of the pits under the spacer feet. It was concluded in Reference 18 that the fretting was occurring at a fairly slow rate. In comparison, under accelerated conditions Larrick and Robinson found 5 to 8 mil deep pits in a pressure tube after 315 days exposure in out-of-reactor tests simulating N Reactor geometries and water chemistry.(19)

During the initial operation of N Reactor a severe vibration problem due to inlet water striking the side of the upstream fuel spacer in the upstream spacer column necessitated the removal of this spacer in all pressure tubes. One spacer was observed by the author to have a hole completely worn through one of the embossed feet (0.11 inch of metal removed). Inspection of the nozzles and pressure tubes during removal of the spacers and closer examination during the Tube 1756 examination did not reveal any significant tube damage due to these upstream vibrating spacers.

Nozzle Examination

Fuel element spacers are 27-1/2 inches long and the feet are 1-1/4 inches from the ends. Most of the larger pits found in the nozzles were grouped at 25-inch (distance between the feet on a spacer) and 2-1/2 inch (distance between feet on two spacers butting end to end) intervals corresponding to the distances between spacer feet indicating the larger pits formed in the crevice areas under the feet. There were only 1 to 2 pits at a location where a spacer foot rested, indicating the pitting occurred at very infrequent intervals. If pitting was occurring continuously it would be expected that new pits would form each time the location of a spacer foot was rotated slightly in the nozzle and eventually would form a ring of circumferential pits at the feet locations. Pitting probably occurred during periods of high oxygen content in the process tube cooling water. This could occur either during single-pass operation with back-up filtered water or when the system was open during charge-discharge operations and oxygen could dissolve in the deionized water. The presence of oxygen will lead to pitting in crevice areas such as those formed by the fuel element spacer feet.

The visual observations, metallographic analyses and the corrosion test in semitreated water all indicate that the pitting corrosion which occurred during reactor prestartup testing when filtered water was passed through the front and rear face piping and nozzles is no longer active. The visual and metallographic data indicate that the oxides are similar in both pitted and nonpitted areas and the corrosion tests indicate that the pitted areas are no more susceptible to subsequent pitting than are the nonpitted areas. However, because of the randomness of possible subsequent pitting, pitting could just as likely occur in an existing pit as elsewhere and the resulting pit could be quite deep. The inactivity of existing pits after being exposed to the high purity deionized water shows that carbon and low alloy steels are a suitable choice as materials in a pressurized water reactor providing proper coolant chemistry is maintained.

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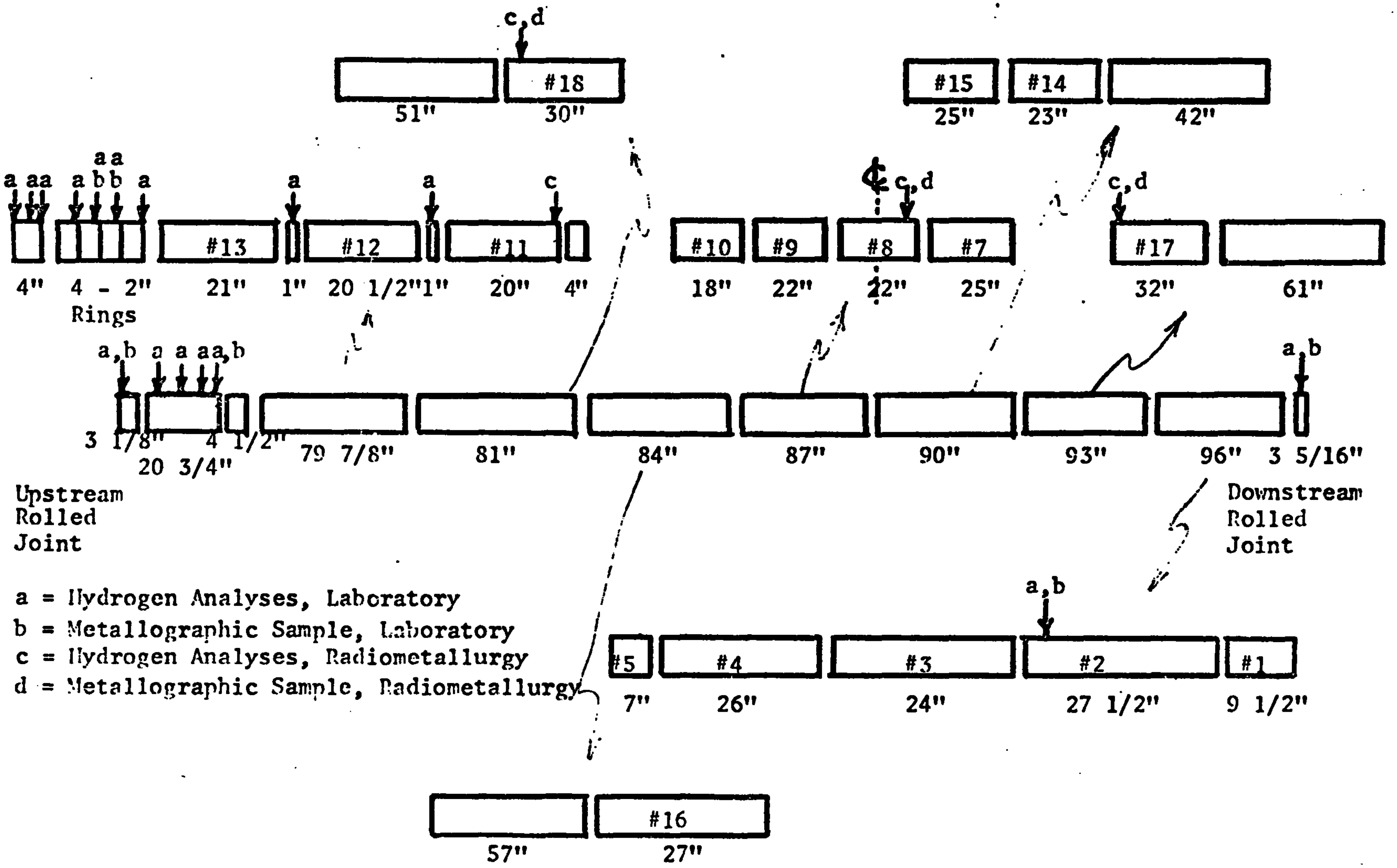


a = Hydrogen Analyses, Laboratory
b = Metallographic Sample, Laboratory
c = Hydrogen Analyses, Radiometallurgy
d = Metallographic Sample, Radiometallurgy

FIGURE 1

Sample Locations - N Reactor Pressure Tube 1756

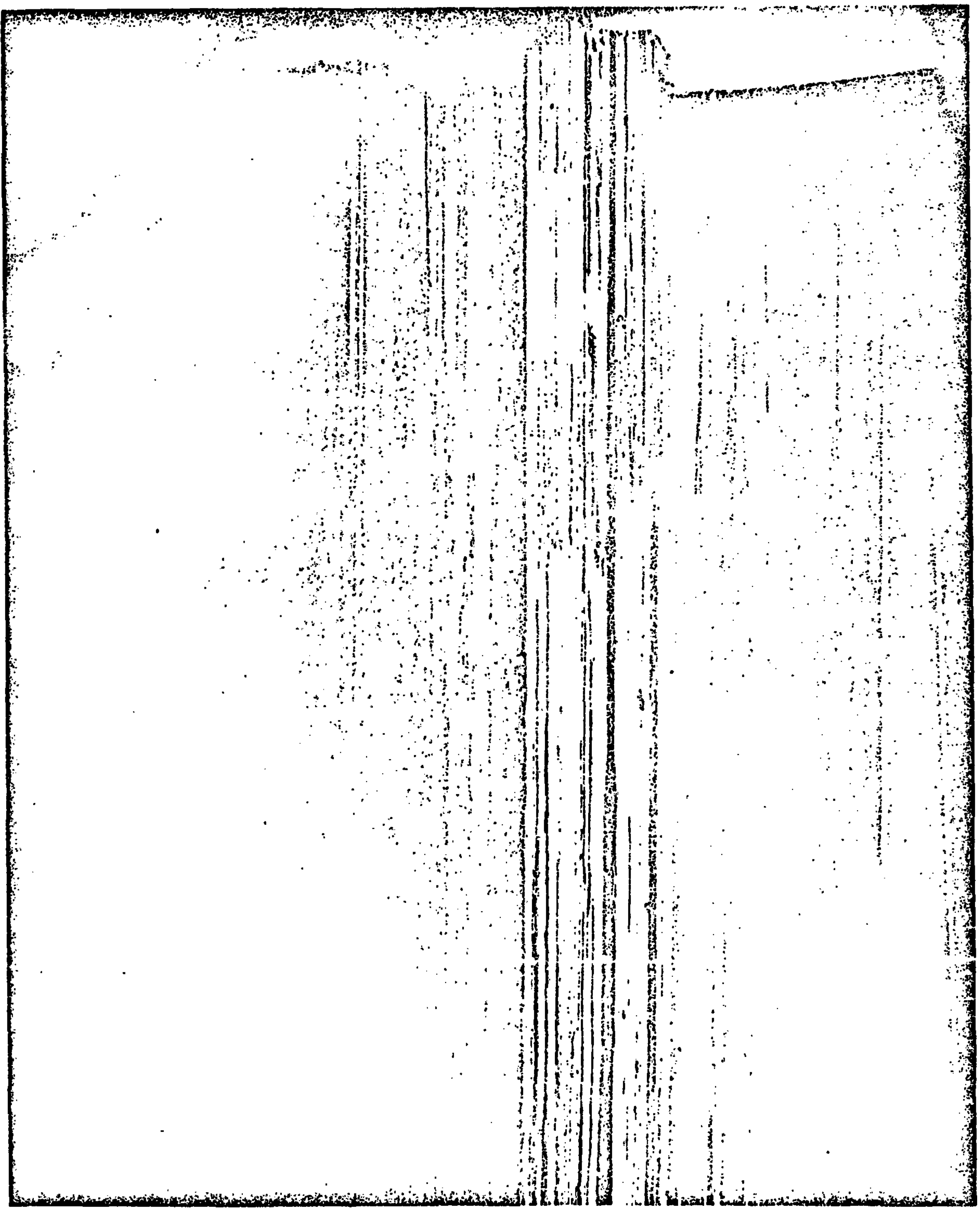


FIGURE 2.

Scratches Near Inlet End, 2X.

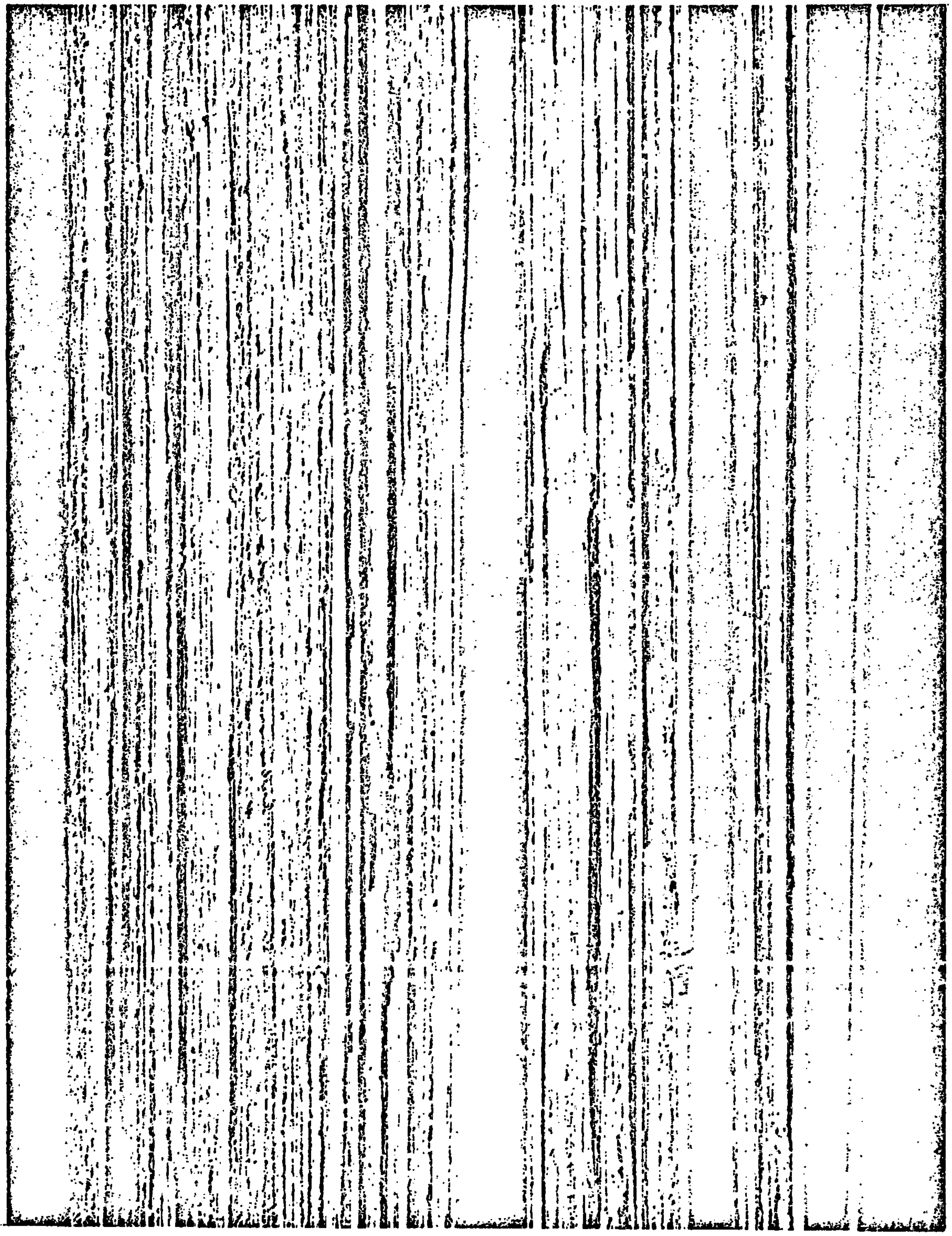
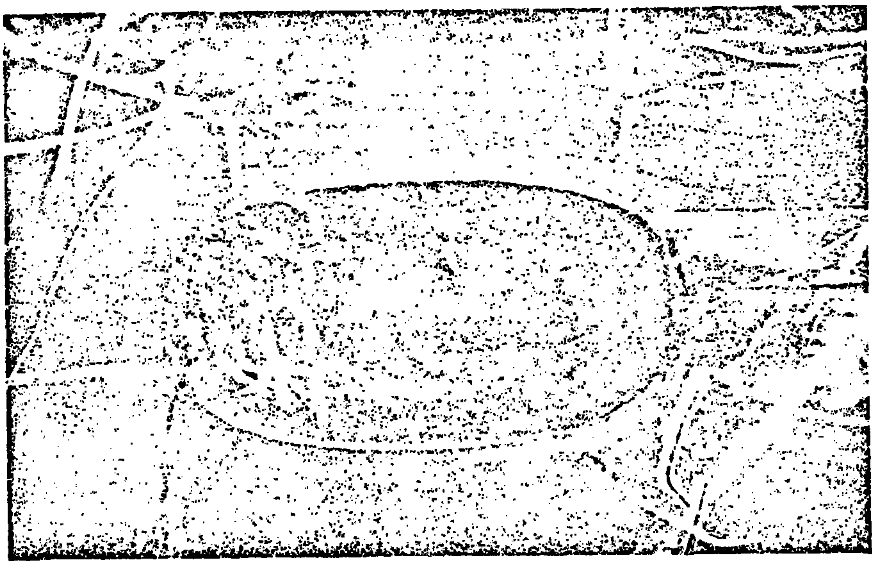
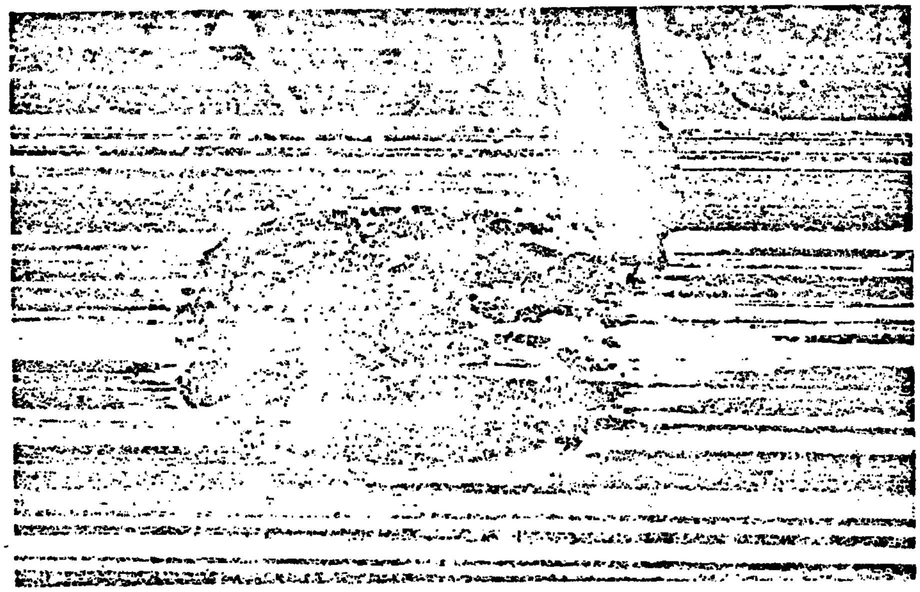


FIGURE 3.

Close-up of Scratched Area, 10X.



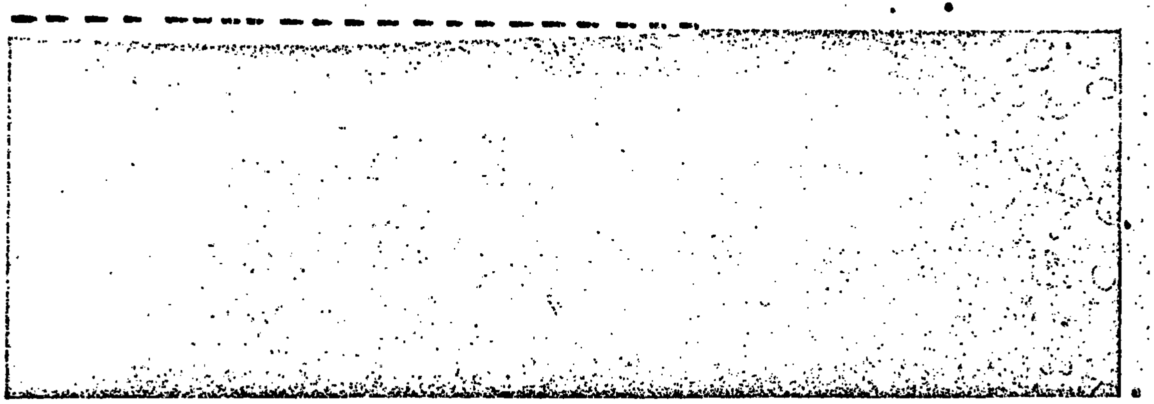
a. Fret Mark at Location No. 3 (See Fig. 1). (5X)



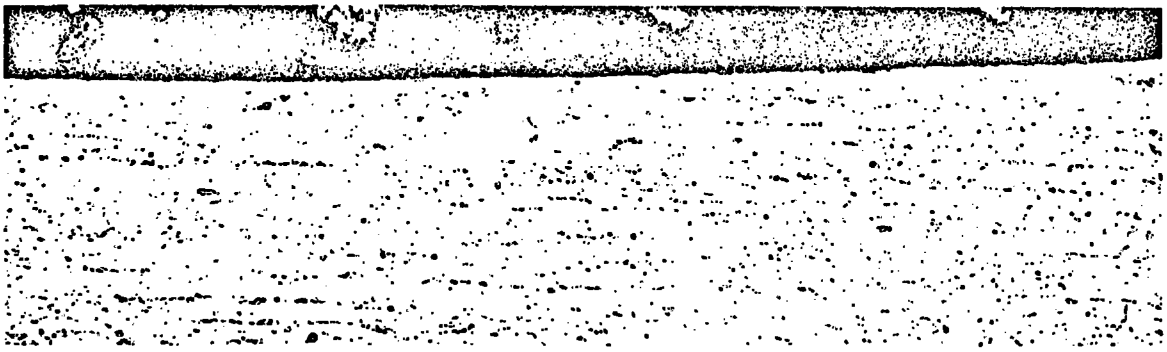
b. Fret Mark at Location No. 4 (See Fig. 1). (5X)

FIGURE 4.

Fret Pits Caused by Fuel Spacer



a. Longitudinal Section, 8X (Dotted Line is Original Surface).

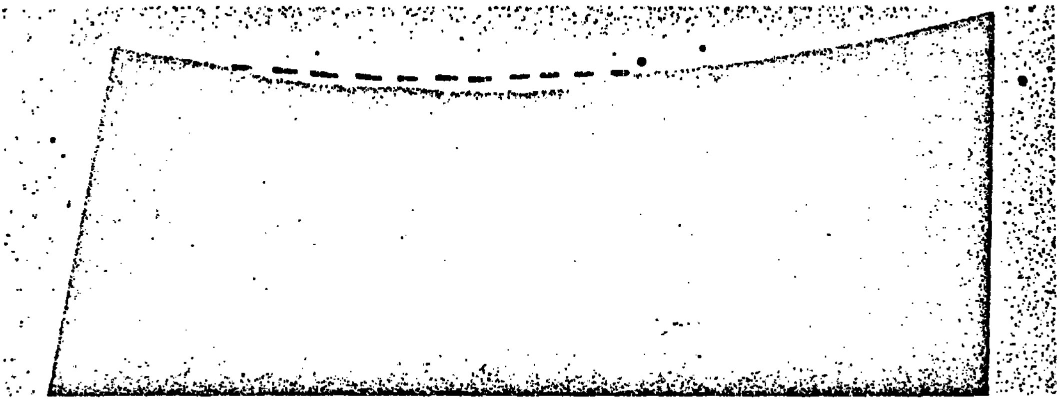


b. Inside Fretted Area, 250X.

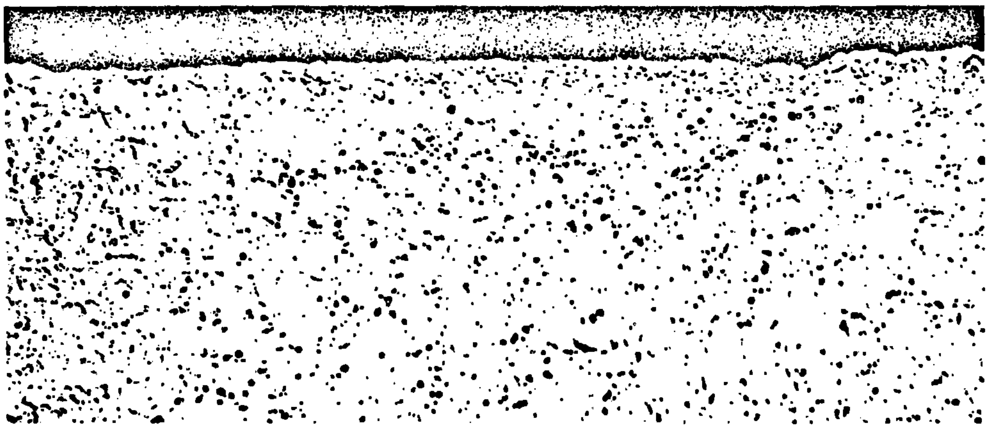
c. Inside Fretted Area, 250X.

FIGURE 5

Fretted Area Due to Fuel Spacer, Location No. 3.



a. Transverse View through Pit, 8X
Dotted Line is Original Surface.



b. Inside Fret Mark, 250X, as Etched.

c. Inside Fret Mark, 250X, Polarized Light.

FIGURE 6

Fretted Area Due to Fuel Spacer at Location No. 4.

FIGURE 7

HYDROGEN CONCENTRATION IN ZIRCALOY-2
PRESSURE TUBE 1756-N

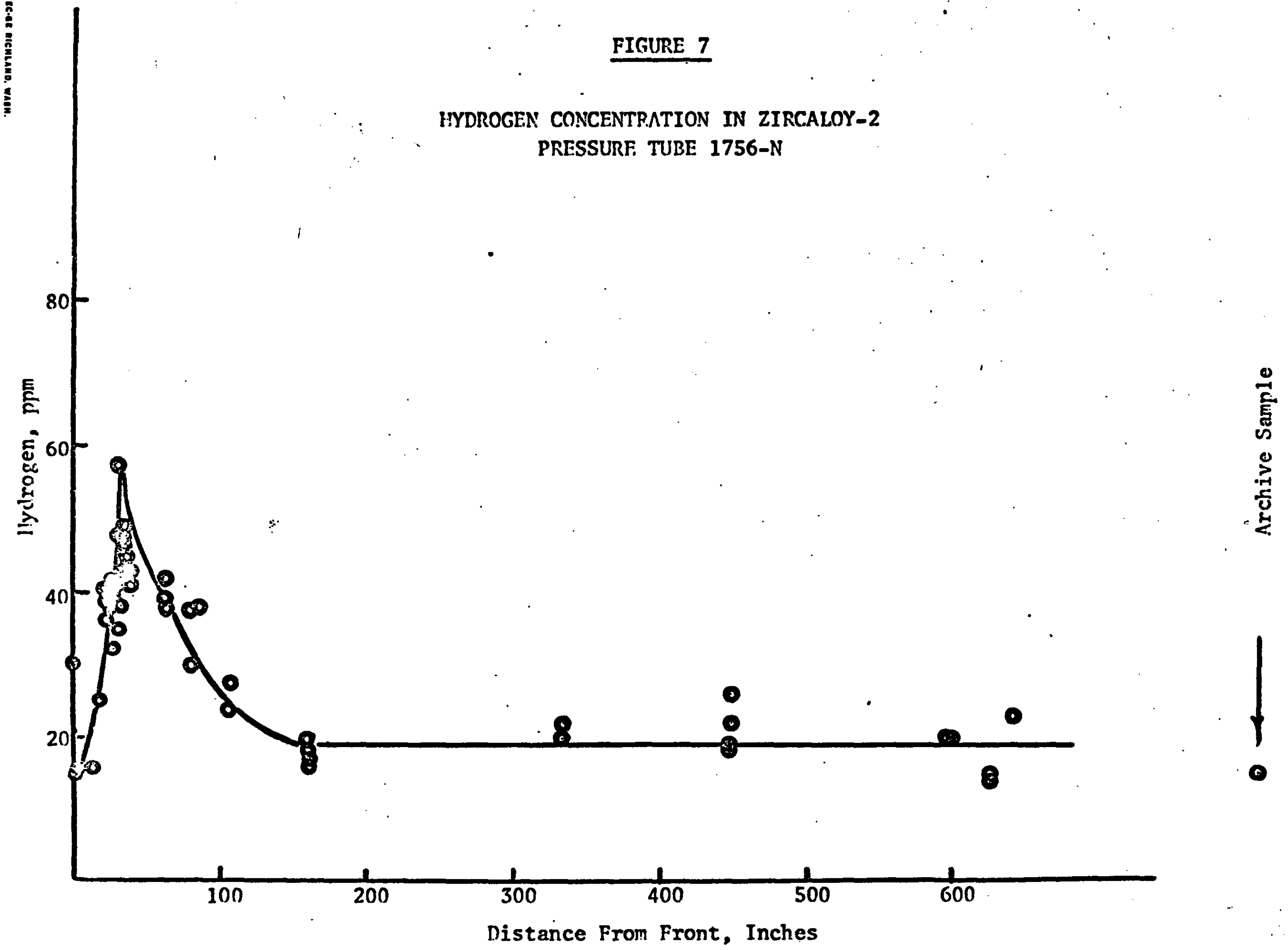
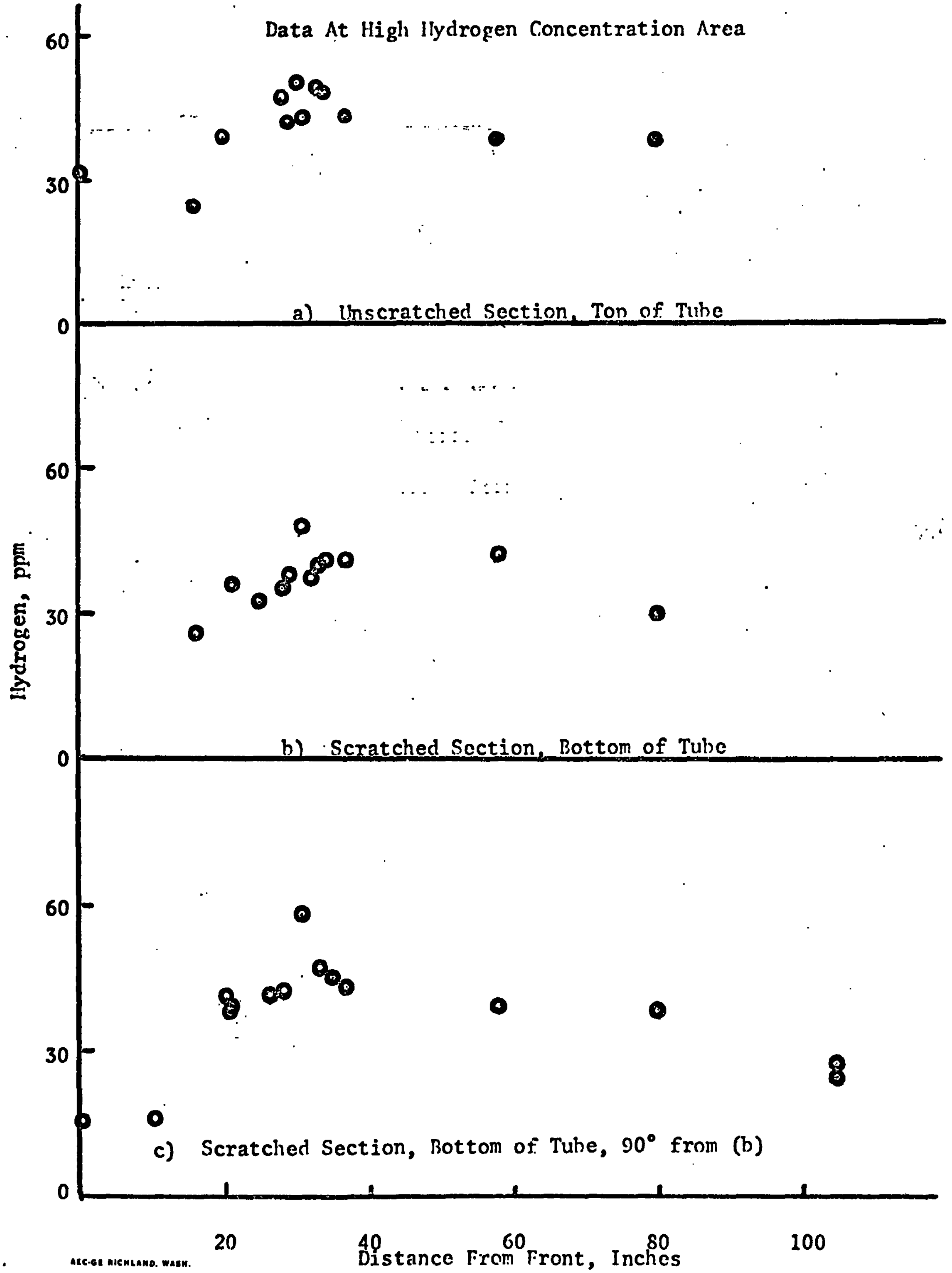
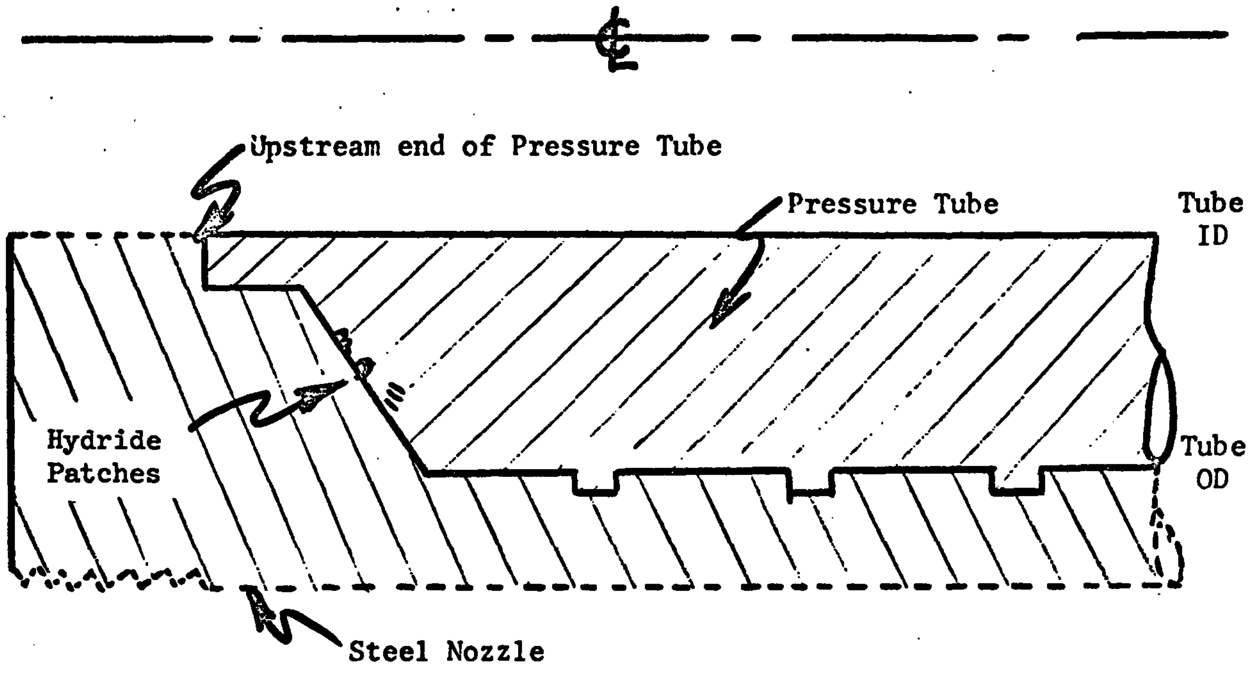


FIGURE 8

HYDROGEN CONCENTRATION - EXPANSION OF FIGURE 7

Data At High Hydrogen Concentration Area





a. Schematic of Rolled Joint Area Containing Hydrides.

b. Largest Patch of Hydride Needles, 500X.

FIGURE 9.

Localized Hydrides in Upstream Rolled Joint Section

FIGURE 10

OXIDE THICKNESS ON ID SURFACE

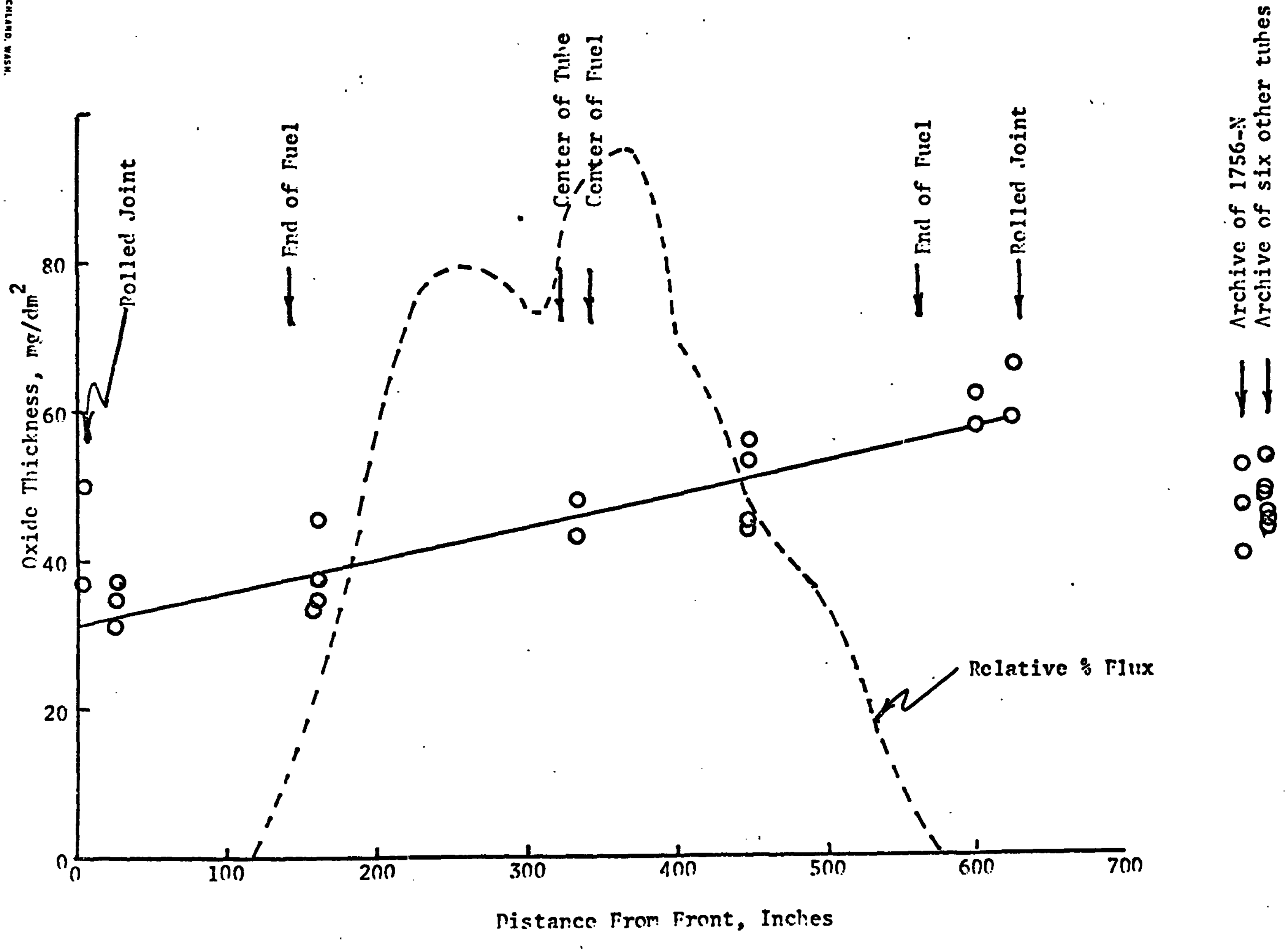
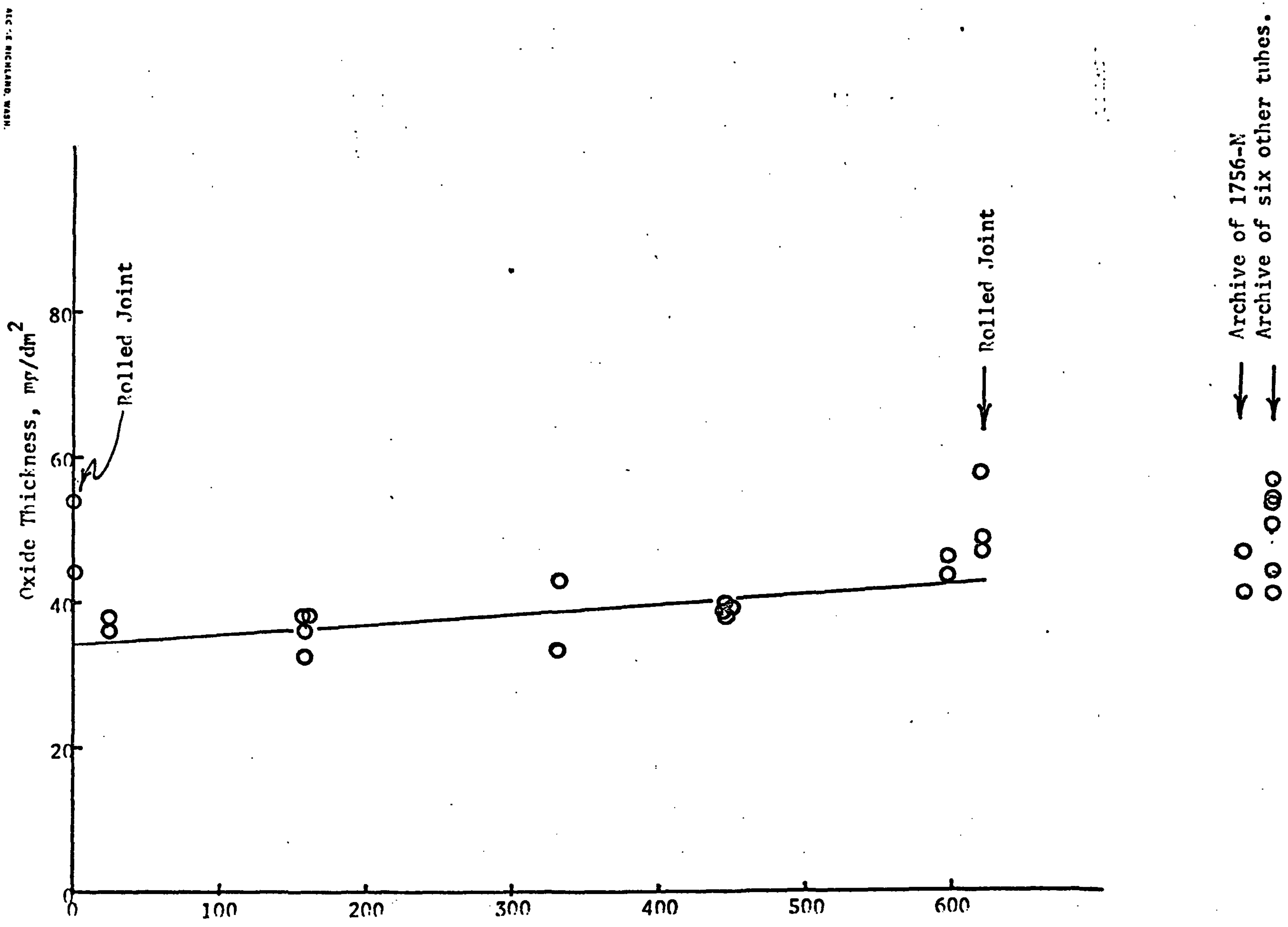


FIGURE 11

OXIDE THICKNESS OF OD SURFACE



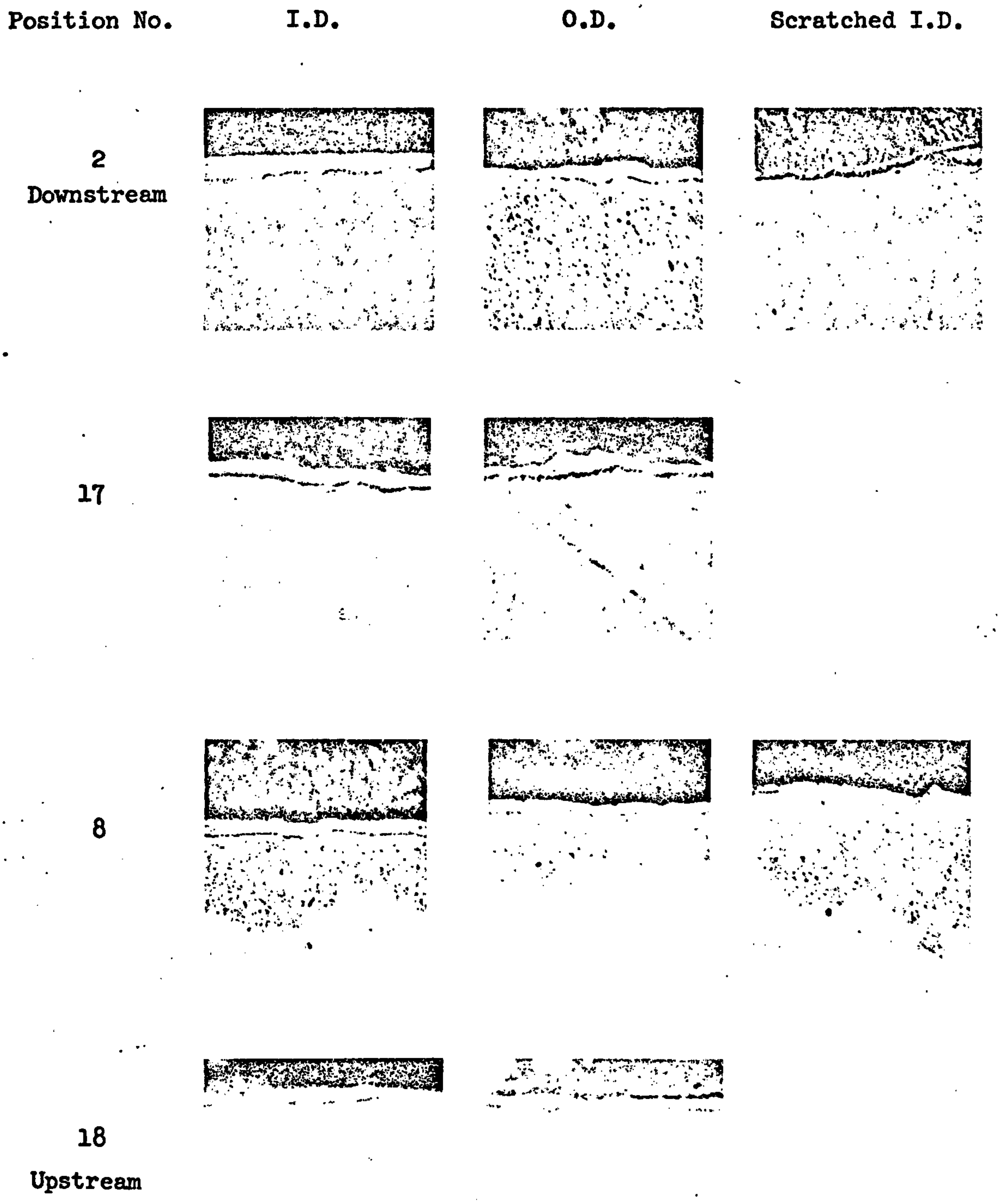
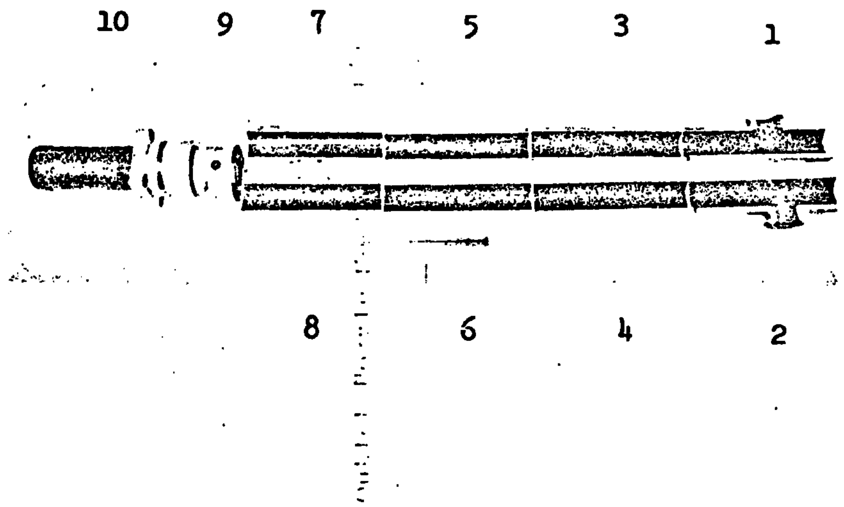
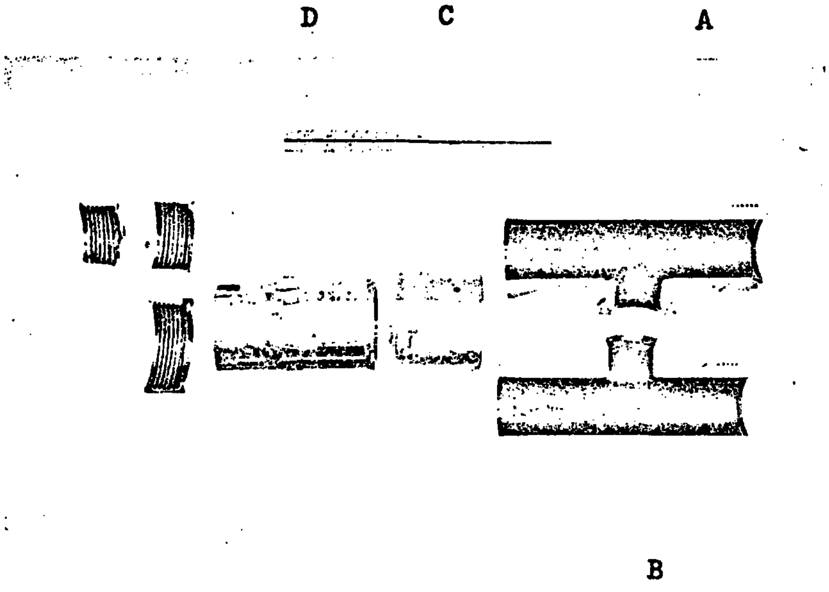


FIGURE 12.

Typical Oxides Formed on Tubing, 750X.



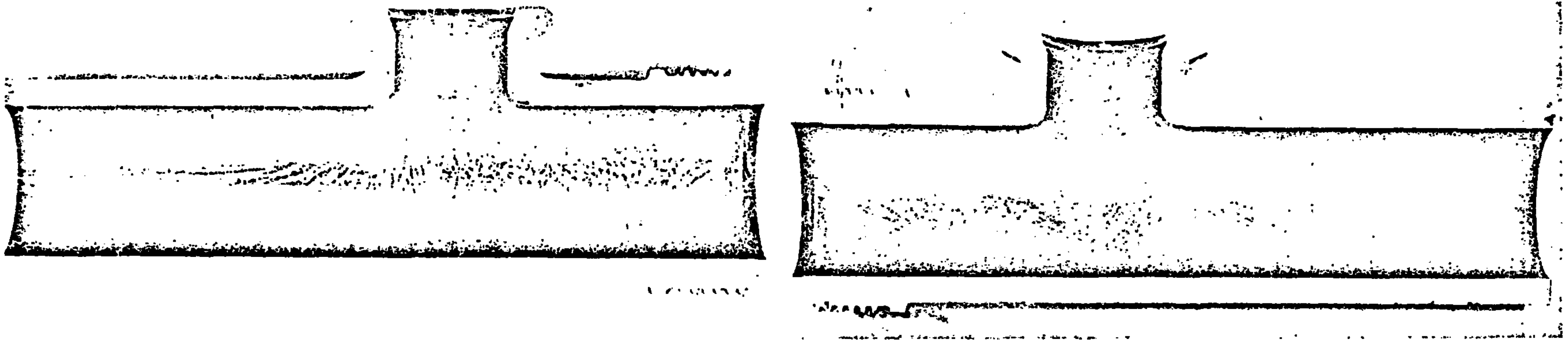
a. Outlet Nozzle, 1/19X.



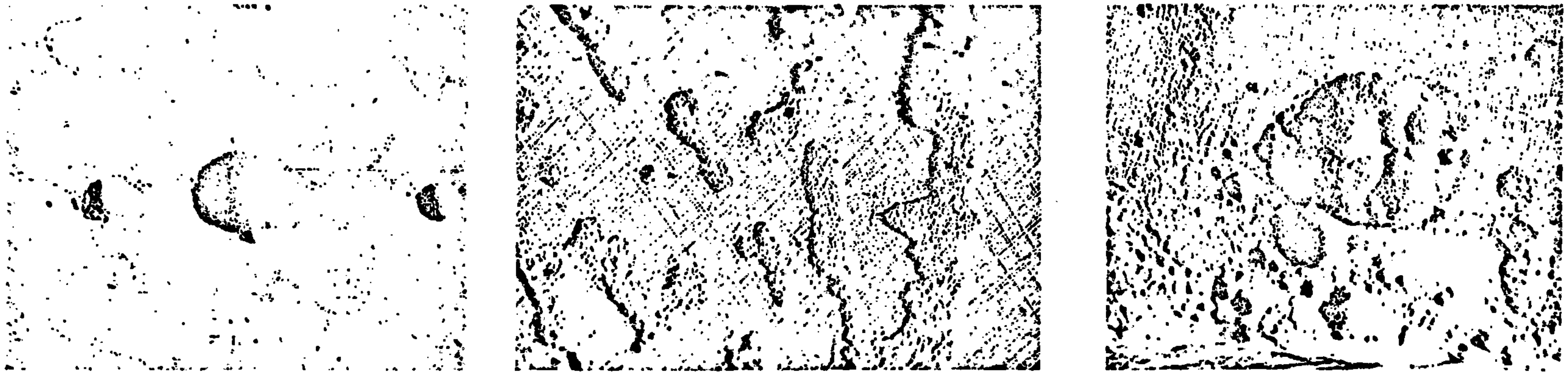
b. Inlet Nozzle, 1/9X.

FIGURE 13.

N-Reactor Nozzles and Identification.



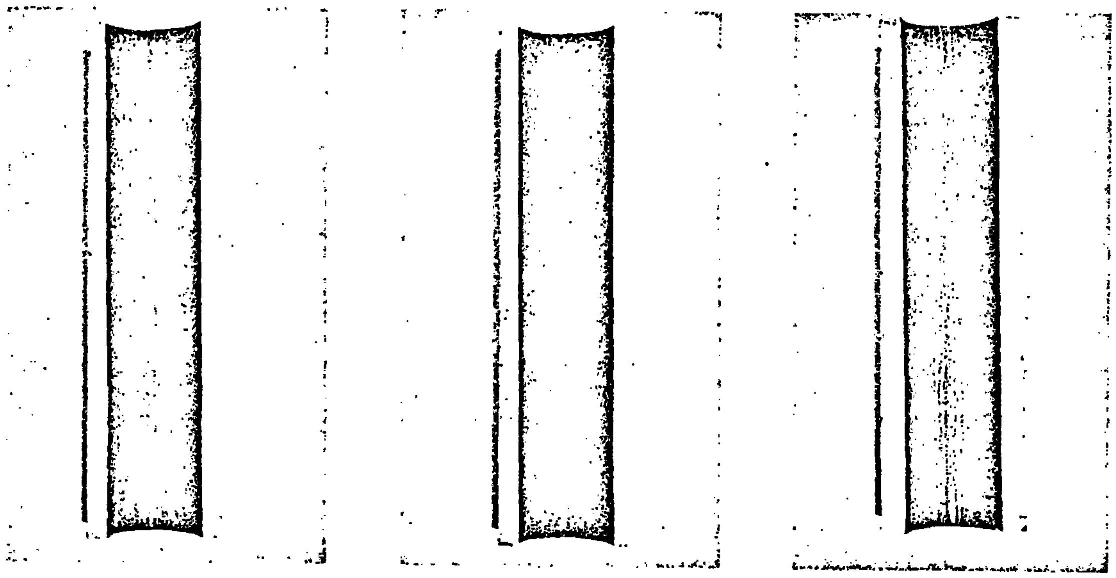
a. Outlet Nozzle Section 1, 1/3X. b. Outlet Nozzle Section 2, 1/3X.



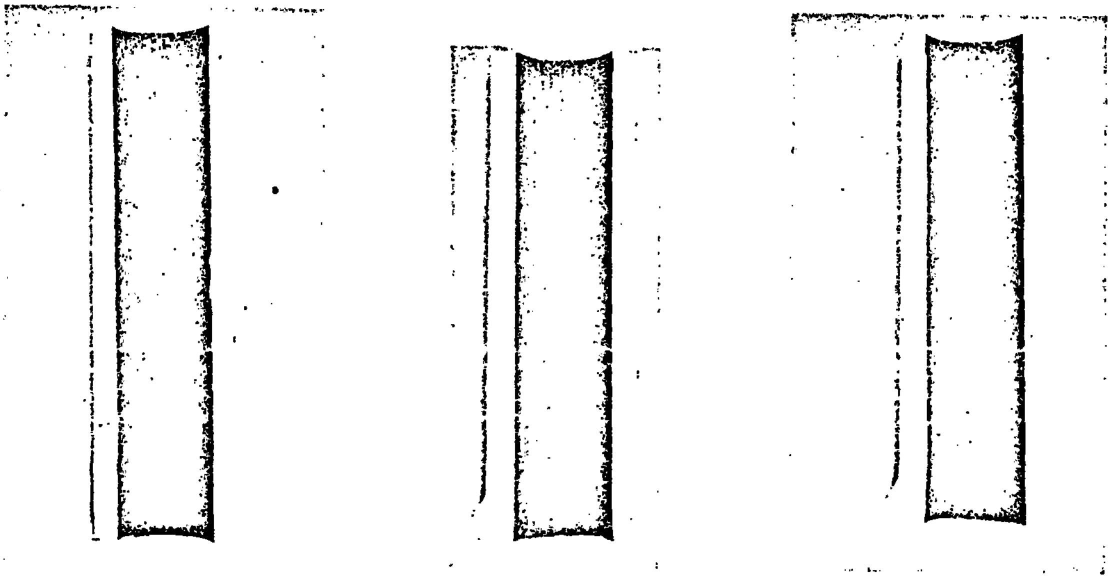
Pit Unassociated with Spacer Contact, Not Typical, 6X. Pit Unassociated with Spacer Contact, Typical, 6X. Pit Associated with Spacer Contact Area, Typical, 6X.

FIGURE 14.

Pitting in Outlet Nozzle.



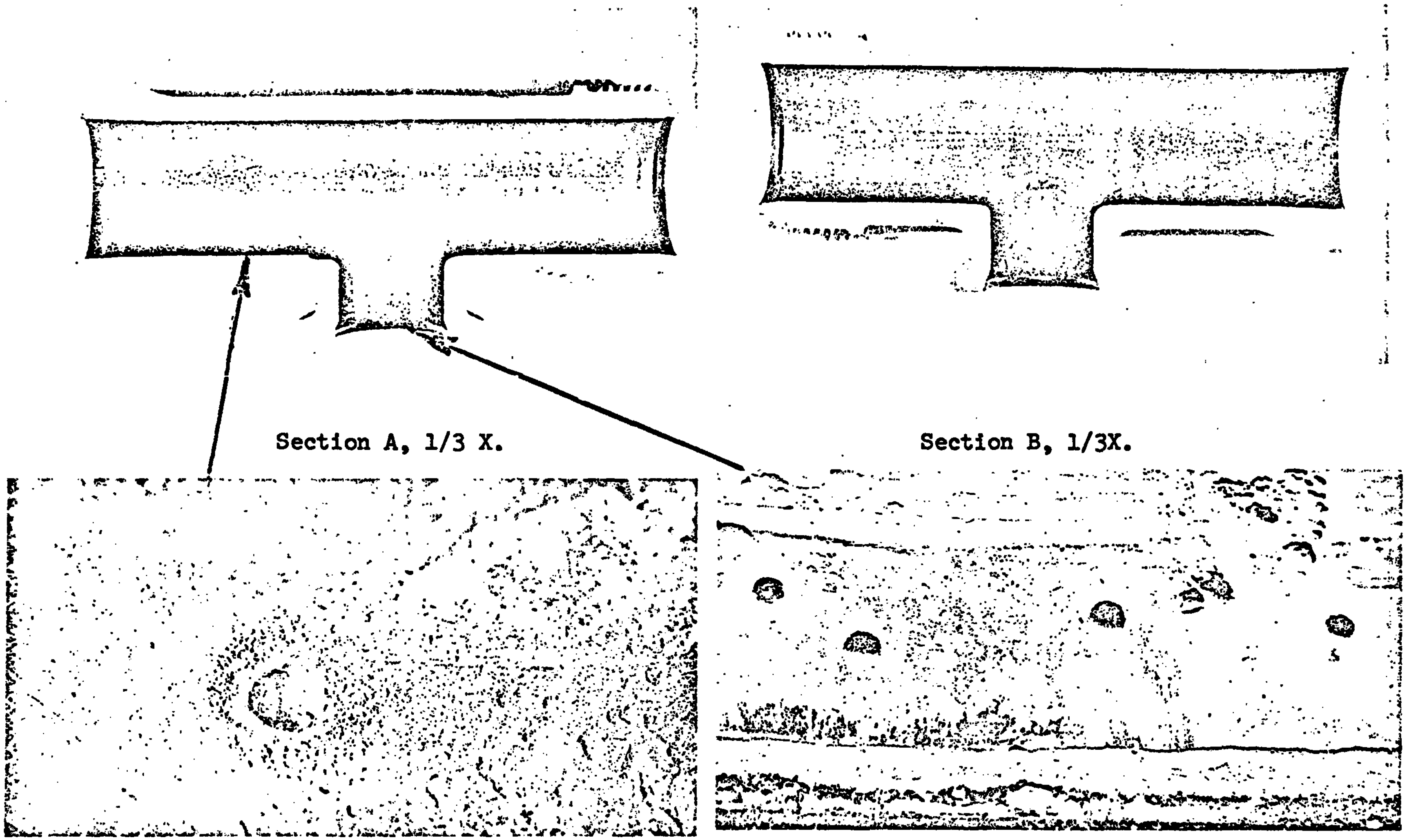
Section 3. Section 4. Section 5.



Section 6 Section 7 Section 8.

FIGURE 15.

Outlet Nozzle Sections, 1/3X.



Section A, 1/3 X.

Section B, 1/3X.

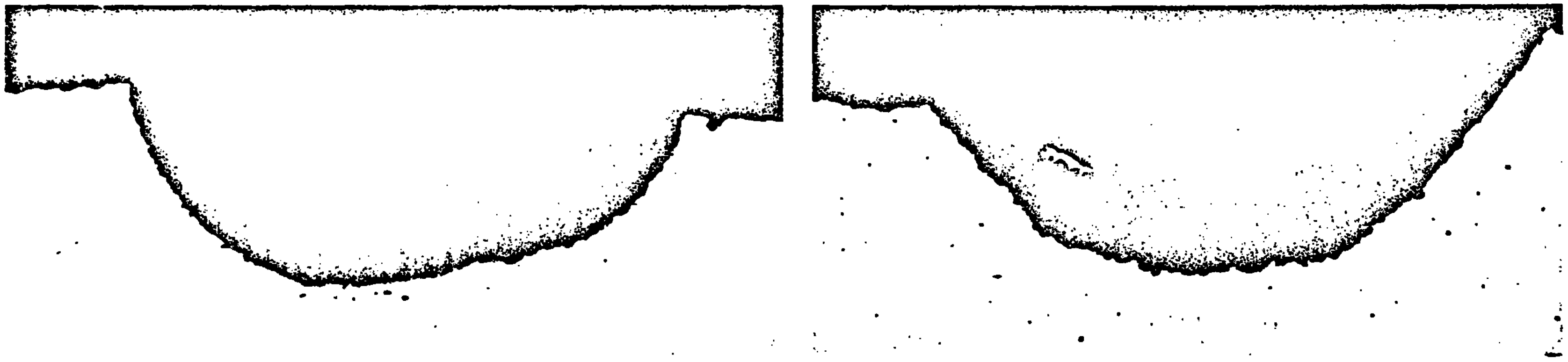
Detail of Large Nontypical Pit, 6X.

Pitting in Gray-Loc Seal Area, 6X.

FIGURE 16.

Pitting in Inlet Nozzle.

Mosaic of Pit in Outlet Nozzle, Section 2.

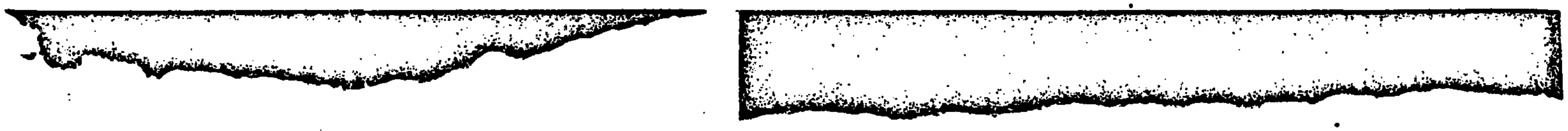


Pit in Inlet Nozzle, Section A.

Pit in Outlet Nozzle, Section 3.

FIGURE 17.

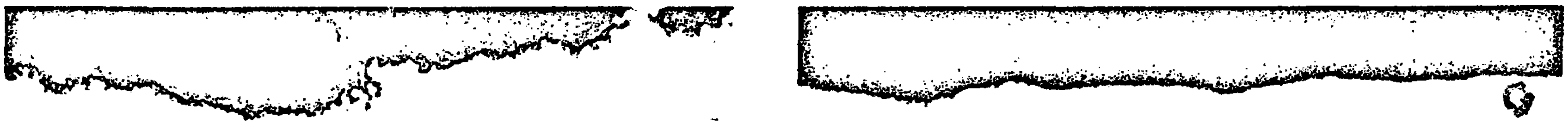
Cross Sections through Largest Pits in Nozzles, 50X.



Inside Pit

Nonpitted Area.

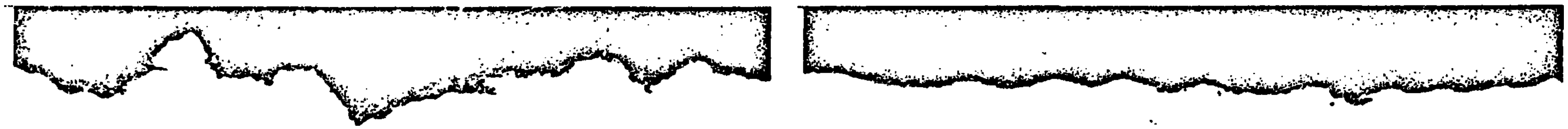
a. Inlet Nozzle.



Inside Pit

Nonpitted Area.

b. Outlet Nozzle.



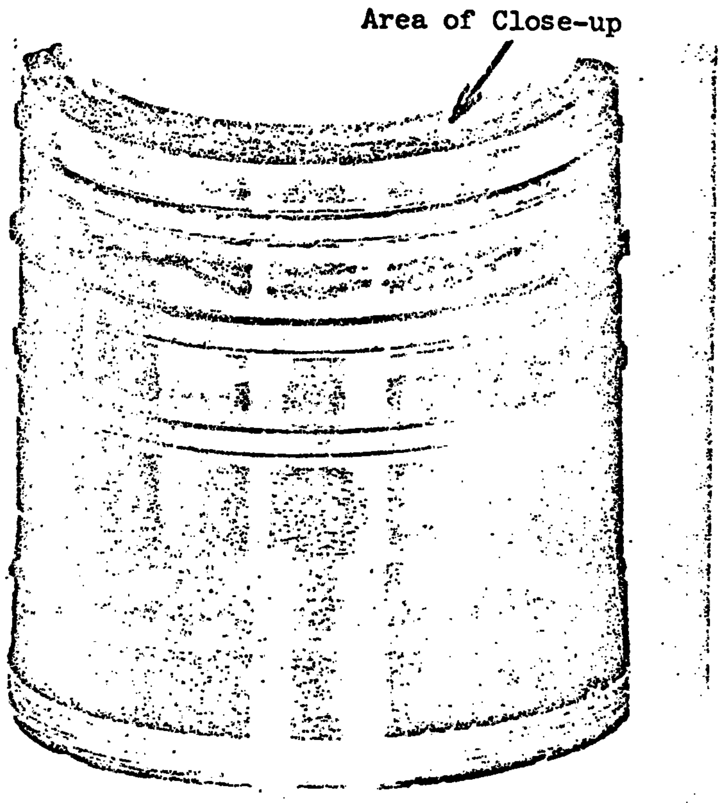
Inside Pit

Nonpitted Area.

c. Outlet Nozzle.

FIGURE 18.

Oxides on Pitted and Nonpitted Areas. (500X)



a. Macro of Rolled Joint, 3/4X.

b. Close-up of Pitting at Steel-Zr-2 Junction, 10X.

FIGURE 19.

Front Nozzle Rolled Joint