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# CORROSION OF STRUCTURAL AND POISON MATERIAL IN SPENT FUEL STORAGE POOLS\*

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## I. INTRODUCTION

At the time most nuclear power plants now operating were conceived and constructed, part of the over all fuel cycle scheme was that the spent nuclear fuel from these plants would be shipped to a fuel reprocessor where the plutonium and other fissionable material would be separated from the radioactive residue. Consequently, a typical nuclear power station is designed to have within its site boundaries, facilities for storing only enough spent nuclear fuel to allow the short lived radioactivity to decay for a period of approximately one year before this fuel would be shipped off-site. For various reasons, it may be necessary at some time during the operation of the reactor, to unload the entire core from a typical nuclear power plant. Consequently, the spent fuel storage pools were designed to hold the amount of fuel discharged in one year (or approximately one-third of a reactor core) plus the entire contents of the reactor core. Recent government decisions, however, have stopped the reprocessing of spent nuclear fuels, and until new government policies are developed regarding long-term storage of the fuel, it has become necessary for the typical utility to store nuclear fuel on-site for much longer than one year. Clearly this situation has required extensive modification and expansion of the on-site fuel storage pools, including the installation in many cases of high density fuel storage racks containing nuclear poisons to prevent accidental criticality<sup>(1)</sup>.

Figure 1 shows a typical reactor spent fuel storage pool arrangement showing the fuel transfer area between the storage pool and the reactor pit. Because the water in the spent fuel storage pool mixes with the primary coolant of the nuclear reactor during fuel unloading and loading processes, it is necessary to maintain the fuel pool coolant to reactor primary coolant specifications. Tables 1 and 2 give the typical spent fuel storage pool chemistry and temperature conditions at a boiling water reactor site where the coolant is high purity neutral water, and at a pressurized water reactor site where the coolant contains dissolved boric acid as a soluble neutron poison. This boric acid in the spent fuel storage pool serves additionally to prevent accidental criticality of the fuel in storage, although no credit for this boric acid is given in the design of the pools.

\*Work performed under the auspices of the United States Nuclear Regulatory Commission

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Materials of construction of spent fuel storage pools are typically stainless steels for the pool liner and most equipment for the cooling system, and stainless steels or aluminum alloys for the fuel storage racks. Nuclear poisons such as boral or a boron carbide organic resin are used between the fuel compartments in some high density racks. The purposes of this paper are three-fold: first, to review the corrosion experience in general of the structural and nuclear poison materials in spent fuel storage pools around the country; second, to describe our in-house experience at the spent fuel storage facilities at Brookhaven on the behavior of the nuclear poison boral and aluminum and stainless steel structures; and third, to present the results obtained at Brookhaven on evaluating the causes of the stress corrosion cracking that occurred in the Three Mile Island - Unit 1 spent fuel storage pool heat exchangers.

## II. STRUCTURAL MATERIALS IN POOLS

The overall performance of structural materials in spent fuel storage pools to date has been excellent. These include stainless steels and aluminum alloys.

### a) Stainless Steels

Stainless steels are used as the liners in spent fuel storage pools almost universally in this country, except for one or two of the very early pools. Most typical spent fuel storage pools have underneath the liner a series of tracer channels in the massive concrete foundation of the pool which serve as a leak detection system should any of the spent fuel pool coolant leak through the liner. These channels divert such leakage to a central header where it can be collected, monitored, and pumped either to a radioactive coolant cleanup system or back into the pool, as the case requires. Although a few stainless steel fuel pool liners have developed leaks at the welds upon initial filling, these were attributed to defects in the original welds, rather than to any effect of the pool environment. Intergranular stress corrosion cracking in the heat affected zone of a weld of a pool liner plate at San Onofre Unit 2 was discovered before the liner was inserted in the pool. This was probably caused by the damp marine atmosphere to which this line was exposed while on storage at the San Onofre site. The only instance of leakage of a pool liner developing after the pool had been in service for a period of time occurred at Salem Unit 1 pool in the Spring of 1979. In this instance, the leakage was small, located with considerable difficulty, and the area dammed off by underwater divers and repaired by welding a plate on top of the leaking area. No attempt was made to determine whether this leak was due to environmental interactions or mechanical failure.

No stress corrosion to date has been detected on any of the fuel storage racks that have been in service, in some instances, for over ten years. However, only visual inspections have been performed on those racks that were removed from service for replacement with newer high density racks.

There have, however, been several instances of stress corrosion cracking of stainless steel piping in the spent fuel pool cooling system, most notably at Three Mile Island - Unit 1<sup>(2)</sup>. At the request of the Nuclear Regulatory Commission, Brookhaven National Laboratory received a portion of the piping from the Three Mile Island spent fuel storage pool cooling system containing a known crack to determine the cause of failure.

The portion of the piping we received is sketched in figure 2. The through-wall intergranular stress corrosion crack, figure 3, occurred in an area adjacent to a weld where extensive amounts of weld repair had been done and large amounts of sensitization occurred. The conclusions of our investigation are summarized below:

1. The primary cause of the cracking appears to be intergranular stress corrosion cracking in the weld sensitized heat affected zone of a weld repair.
2. Although no definite corrosive species were identified as the cause of the cracking, the various traces of Cl on both the pipe inside surface and in the areas of the crack fracture faces determined by EDX scans and the inside surface etched grain boundaries is evidence of etching and possible contamination of the system by Cl ions perhaps during a cleaning or pickling operation. The significance of Al, Si, Ca, P and K is not currently obvious.
3. The significance of the widely dispersed MnS stringer-like inclusions as pit nucleation sites is inconclusive. Also, importance of the widely dispersed sulfur traces throughout the fracture face is yet to be determined, but seemingly requires further investigation into the effects of both S and MnS in the spent fuel environment.
4. The results of Electrochemical Potentiokinetic Reactivation Analysis (EPR) did show at least one area of the pipe's cross section had been sensitized significantly by the welding process which is a reasonable indication of the pipe's precracked condition.
5. It is evident from the Constant Extension Strain Rate Tests (CERT) results (corroborated by the oxalic acid etched microstructures) that the Type 304 SS material, with its high (0.07%) carbon content and complex thermal history (2 repairs) was severely sensitized at various locations about its girth. This degree of sensitization was sufficient to cause intergranular-type fracture of this material during CERT testing in air at a strain rate of  $8.6 \times 10^{-6} \text{ sec}^{-1}$ . This degree of sensitization coupled with the residual stresses of welding and the possible contamination of Cl ions was seemingly sufficient to crack the piping by an intergranular stress corrosion cracking mechanism.
6. A reasonable explanation of the intergranular-type cracking observed in the CERT tests (in air) can be made that is similar to that postulated by Hipsley, et al.<sup>(3)</sup> It is possible that at some critical strain, the MnS/TiC inclusions start to decohere from the matrix alloy. Since the 304SS was significantly sensitized (grain boundary carbide formation) this decohesion (ductile in nature) started to apply a shear stress across the more brittle carbides in the grain boundaries causing them to "slide" across one another thereby resulting in the intergranular-type failure with the facets appearing in a dimpled rupture mode. This theory is somewhat substantiated by the fact that the intergranularly failed specimens tested in solution or air, all exhibited a similar degree of elongation (strain) of almost 50% and fell within a reasonable scatter band for tensile stress 66-82 ksi, which is quite similar to the specimens which failed in a purely ductile manner.

It is obvious from these investigations that, even in the relatively benign environments and low temperatures at which the spent fuel storage pool operates, care should be taken in manufacturing or fabricating stainless steel components to prevent undue sensitization of the stainless steel, high stresses associated with weld repair areas, and contamination of the pool with harmful impurities such as sulfur compounds or chloride compounds.

#### b) Type 17-4 PH STAINLESS STEELS

Type 17-4 PH stainless steels are used in a number of spent fuel storage pools as seismic restraints in order to provide stability to the racks. In this application, the normal load on this material is well below yield, and produced only by nut tightening or bolting stresses. However, the loads on these bolts may approach their design strength during a design basis earthquake for a short period of time. Consequently, there is considerable interest in the long-term performance of this material in a spent fuel storage pool environment. Further, there is a temptation on the part of engineers to make the material as strong as possible by heat treating it to the H-900 condition.

The literature contains many references to stress corrosion cracking of Type 17-4 PH in the H-900 condition. However, almost exclusively these references are to exposures at temperatures of 149°C (300°F) or higher. In a marine atmosphere, this material has failed in the H-900 condition at temperatures up to 52°C (125°F) but not when immersed in sea water at temperatures of 27-30°C (80-85°F).<sup>(4)</sup> Clearly the situation is somewhat clouded as to whether or not this material in this heat treatment might crack over long periods of time in spent fuel storage pool environments. Most utilities are now recommending the H-1025 or the H-1100 heat treatment for this material, under which condition it has operated satisfactorily in many applications at temperatures and pH quite consistent with that present in both BWR and PWR spent fuel storage pools. In the High Flux Beam Reactor at Brookhaven it has performed well in a pH 5.0, high oxygen environment at 21°C-68°C (70-155°F) for over 15 years, where this material is used in the control rod drive pinions.

The second potential problem with the use of this material in spent fuel storage pools comes from reactions involving the heat treatment scale usually present on components of 17-4 PH following the H-1100 heat treatment. The manufacturers of the material recommend that the heat treatment scale be removed by chemical cleaning or by mechanical means before the materials are used in a water environment. Certainly any residual scale on the material could potentially lead to pitting in the long-term in an oxygenated environment. We exposed several specimens of this material with the heat treatment scale intact to the spent fuel storage pool at the High Flux Beam Reactor at Brookhaven to determine the long-term behavior of the heat treatment scale. Figure 4 shows that in six months the surface of the 17-4 PH exposed with the heat treatment scale intact was heavily coated with a brown rust, whereas, the surface of the specimens cleaned after heat treatment remained bright and shiny. In neither case, however, was there any measurable general corrosion, although there was possibly some slight pitting underneath the rust on one specimen. Since this rust-like



material would contribute to the crud deposits on the floor of the spent fuel storage pool and might in some areas lead to localized attack on the 17-4 PH, removal of the heat treatment scale from any components of this material before their insertion into a spent fuel storage pool would seem prudent.

#### c) Aluminum Stainless Steel Junctions

Aluminum components have stood up well in spent fuel storage pools, particularly in those associated with boiling water reactors in which the environment is basically neutral, high purity water. However, in a boric acid pool, or even in a neutral water pool there is always a potential for pitting of the aluminum at a point of galvanic contact between aluminum and stainless steel. At some reactor sites, notably Vermont Yankee<sup>(5)</sup>, insulating feet have been put on the aluminum racks where they sit on the stainless steel floor of the spent fuel storage pool to minimize this pitting attack. In the spent fuel pool associated with the High Flux Beam Reactor at Brookhaven, we have aluminum racks and a concrete floor in the pool over which is laid a 1/4" stainless steel sheet to prevent damage to the concrete. Typical water chemistry in the pool is similar to that in Table 1. To monitor the pitting reactions that might be occurring between aluminum racks and the stainless steel floor of the reactor pool, a series of corrosion coupons have been kept immersed in the pool for several years. Figure 5 shows the extent of pitting of the aluminum surface following removal from the pool after six months exposure. The pitting occurred only around the edges of the point of contact between the aluminum and the stainless steel. The inner portion of the sandwich, while slightly discolored, shows no pitting attack, which is probably due to the reduced availability of oxygen in this area. In February, 1979, while these specimens were present in the pool and while the mixed bed in the pool water purification system was being regenerated, a faulty shut-off valve allowed some of the 5% sulfuric acid regenerating solution to leak into the pool. The pH dropped to 3.6 and the resistivity of the water to 1,000 ohm-cm. Approximately a five fold increase in the aluminum concentration of the water was observed. After a week of operating the demineralizers and the purification, the pH had risen to 5.2 and the resistivity to 210,000 ohm-cm. The pH had returned to the normal range within 11 days. The samples were removed, and the three pits shown in figure 5 were reexamined. No new pitting was observed as a result of this incident, although the three pits shown in the figure did grow slightly. Subsequently, several of the aluminum racks were removed from the pool (as part of our in-house replacement of the fuel storage system with high density fuel storage racks) and examined. Again, there was pitting of roughly the same magnitude shown on the photograph at several places on the feet of the racks, where they were in contact with the stainless steel liner of the pool. However, in no way did this minor pitting affect the structural integrity of the racks over the period of 15 years since they were installed in the pool and the pool filled.

Several of the boiling water reactors have replaced their aluminum racks as part of the densification program, and no significant corrosion has been observed where the aluminum racks rested on the stainless steel floor of the pool.

### III. POISON MATERIALS IN POOLS

The extensive use of nuclear poisons, especially boral in spent fuel storage racks, has been brought about by the need for increasing the storage capacity of the various nuclear power plant sites. The literature on boral, dating back over a period of 20 years, states that its corrosion resistance is the same as that of the aluminum cladding, provided the  $B_4C$ -Al cermet in the core of the boral is not exposed to the coolant. Figure 6 shows a schematic of boral. As can be seen, it consists of an aluminum boron carbide cermet clad on both sides and along the edges with aluminum, typically either 1100 or 6061 alloy. Because of this precaution in the literature, (which experience has shown to be unnecessary) all boral exposed in the commercial nuclear pools was originally designed to be contained in sealed compartments between the fueled storage cells within the racks to prevent access of water to the boral.

#### a) Compatibility of Boral with Water

At Brookhaven, boral has been exposed in the fuel storage area of the Brookhaven Medical Research Reactor to water of essentially the same quality as that in a BWR pool since January, 1959. In the Summer of 1978, because of the interest in the use of this material in spent fuel storage pools, several punchings were taken from the boral plates in this reactor as shown in figure 7, and analyzed metallographically in our laboratory, and for boron at the University of Michigan by neutron attenuation. Figure 8 shows that the neutron attenuation data for all six specimens agreed within 20%, which is probably within analytical error for such small samples. Specimen #5 was analyzed chemically to contain 41.3%  $B_4C$  in the core, which is in the upper range of boron concentration for material produced in the 1950's. Additional portions of these punchings were examined by General Electric in San Jose. It is clear from these examinations that there has been no loss of boron carbide to the coolant of the Brookhaven Medical Research Reactor over the period of more than 19 years that this boral was exposed to the coolant. This observation gives considerable assurance that, should spent fuel pool water leak into the cavities containing boral, there will be no concomitant loss of the boron carbide from the cavity.

#### b) Swelling of Poison Racks

At several nuclear power stations, when racks were inserted into the pool containing boral sealed in stainless steel cavities, leakage of water into the stainless steel cavity containing the boral led to a formation of hydrogen by the initial passivation corrosion of aluminum. Production of hydrogen during this period, of course, has been known for a long time. Figure 9 gives some data published by Draley and Ruther in 1953<sup>(6)</sup> showing that the amount of corrosion in terms of metal lost over the first week or so after aluminum is exposed to water, can equal as much as 20 mg/dm<sup>2</sup>. In terms of hydrogen produced by this reaction, this corrosion could produce as much as 7500 cc of hydrogen at standard temperature pressure conditions per tube of the spent fuel storage module. In as much as the void space around the boral, where it is sealed into the tube, is of the order of 100-150 cm<sup>3</sup>, this quantity of hydrogen is quite sufficient to produce the 5-6 psi pressure needed to bulge the thin stainless

steel cladding that seals the boral in place. The implication of this phenomenon will be discussed later in this session by Mr. Vincent<sup>(7)</sup>. Since it is impossible to ensure that all of the boral will be permanently sealed, it is desirable to vent these cavities intentionally so that the hydrogen produced can be released to the environment without allowing swelling of the racks. This solution to the swelling problem, however, places greater emphasis on the possible corrosion that might occur where aluminum and stainless steel come in contact in the spent fuel coolant. This is of particular concern in the pools adjacent to PWR's, where the coolant contains boric acid at a pH of around 5, as shown in table 2. Based on our experience with coupons, described above; the pitting will primarily occur near the points where the boral-containing cavities are vented. Since these cavities are as much as 20 feet long, significant loss of aluminum from the pitting is unlikely. Further, from the BMRR experience, and from studies of this pitting corrosion under extreme conditions of low pH and elevated temperature, it is very unlikely that the boron carbide itself would be lost by the pitting corrosion. Measurements of pitting currents in this couple have been shown to be strongly affected by the amount of oxygen available at the site where the active pitting is occurring. Further, the aluminum hydroxides produced by the pitting corrosion would be expected to remain in the cavities and hold the B<sub>4</sub>C particles in place.

Most of the utilities utilizing the vented boral racks have committed themselves to a corrosion monitoring system consisting of both small coupons that are vented to the environment and full length tubes containing the boral<sup>(8)</sup>. Since small coupons will have much greater access to oxygen at the point where the aluminum and the stainless steel are in contact in the environment, we think they will give a conservative measure of the state of the nuclear poison throughout the storage racks.

#### IV. CONCLUSIONS

- a) The performance of structural and poison material in spent fuel storage pools to date has been excellent.
- b) Intergranular stress corrosion of sensitized stainless steel can occur in these environments if the material is heavily sensitized and heavily stressed, as might occur in areas with extensive weld repairs.
- c) Accidental contamination of the pool with materials such as chloride or reduced forms of sulfur could lead to initiation of stress corrosion cracking of such materials. Clearly careful quality construction techniques are recommended.
- d) Boral can be exposed to nuclear coolant without detectable loss of the boron carbide from the matrix.
- e) Pitting corrosion of the aluminum cladding on the boral, however, is possible where the cladding is in contact with stainless steel, especially at those points of contact where access to oxygen is highest, and in pools containing boric acid. This pitting should not effect the poison capability of the boral and should not in any way dissolve or corrode the boron carbide particles themselves.

f) Pitting of aluminum racks, where they are in contact with stainless steel can occur. However, this pitting to date in racks removed from several reactors in which the pools contain high purity water has not produced significant degradation of the rack materials.

g) Type 17-4 PH stainless steel should be used in the H-1025-1100 condition and the heat treatment scale removed by either chemical or mechanical means to avoid possible stress corrosion cracking, pitting, and sludge formation in the pool.

#### V. ACKNOWLEDGEMENTS

This work was performed under the auspices of the U.S. Nuclear Regulatory Commission, which also provided us with the samples of the Three Mile Island spent fuel pool piping system for examination. The assistance of Mr. R. Karzmar of Brooks and Perkins, Inc., in obtaining the neutron attenuation and chemical analyses of the boron punchings from the BMRR is gratefully acknowledged. The assistance of C. Schnepf and W. Lindsay in performing the laboratory investigations at Brookhaven, the assistance of the Reactor Division staff in obtaining the punchings from the Brookhaven Medical Research Reactor for this investigation and in performing the corrosion monitoring studies in the High Flux Beam Reactor spent fuel storage pool, were all essential to this evaluation.

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6. J. E. Draley and W. E. Ruther, Report ANL-5001, Feb., 1953.
7. D. M. Vincent, Monticello Spent Fuel Storage Module Corrosion Experience, this symposium.
8. i.e. Commonwealth Edison, Co., Zion Units 1 and 2 and Dresden Units 2 and 3 Spent Fuel Pool Modifications, Public Service Electric and Gas, Salem Unit 1 Spent Fuel Pool Modification; see also ref. 7.



TABLE I

## BWR Spent Fuel Pool Chemistry\*

	Specification	Typical Range
Conductivity ( mho/cm)	<5	<1
Chloride (ppm)	<0.1	<0.04
pH	5.6-8.6	end of lower range
SiO <sub>2</sub> (ppm)	<0.5	.1-.5
Temperature	<52°C (<125°F)	37°C (93°F) 8/15/90

\*Courtesy Commonwealth Edison, Co., Dresden Station

TABLE II

## PWR Spent Fuel Pool Chemistry\*

	Specification	Typical Range
Boric Acid, as ppm Boron	>2000	2300
Chloride (ppm)	<0.15	<0.10
F <sup>-</sup> , ppm	<0.15	<0.02
pH	4.0-7.0	4.7-5.2
Temperature	<65°C (<150°F)	18-29°C (65-85°F)

\*Composite of data from Portland General Electric Co.,  
Trojan Specifications, and Metropolitan Edison Co.,  
Three Mile Island - Unit 1 Sampling

were reduced for preprint production.  
Magnification may be less than that  
shown in the figure caption.

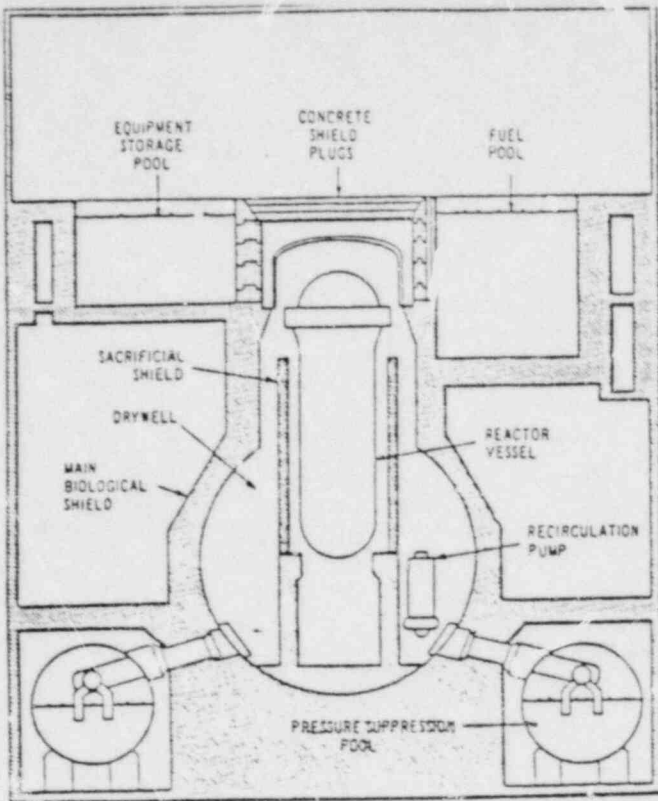
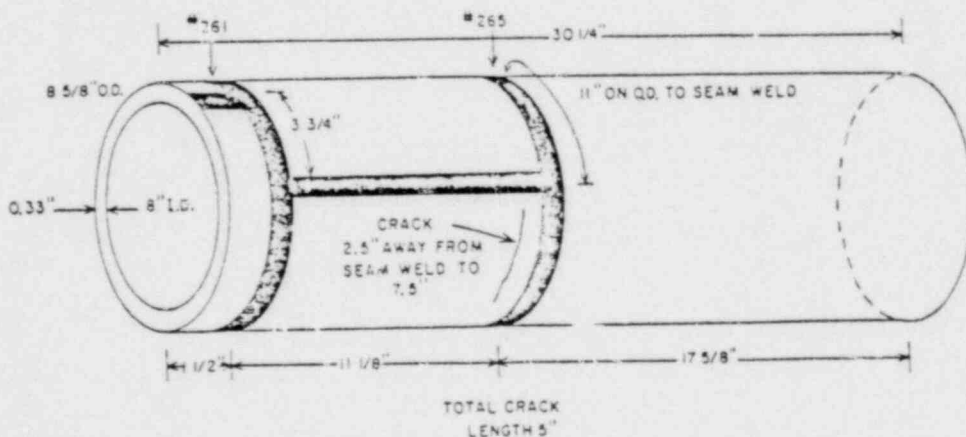


Figure 1

Arrangement of the spent fuel pool and reactor vessel cavities in a typical BWR. During refueling, the reactor vessel cavity is flooded to height of the water level in the fuel pool and gates open between them to permit under water handling of fuel. From the GE BWR Self-study course.



3 MILE ISLAND PIPE  
MET. ED.  
SCH. 40 TT 304  
HT 334165  
BAL. OF 24' 1 3/8"  
W 18809

Figure 2

Location of welds and crack on 30 1/4 inch piece of 8 inch stainless steel pipe: Three Mile Island unit 2 spent fuel pool piping.

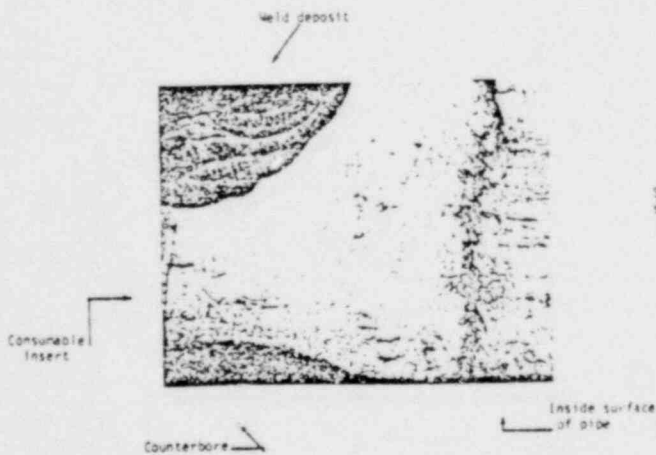
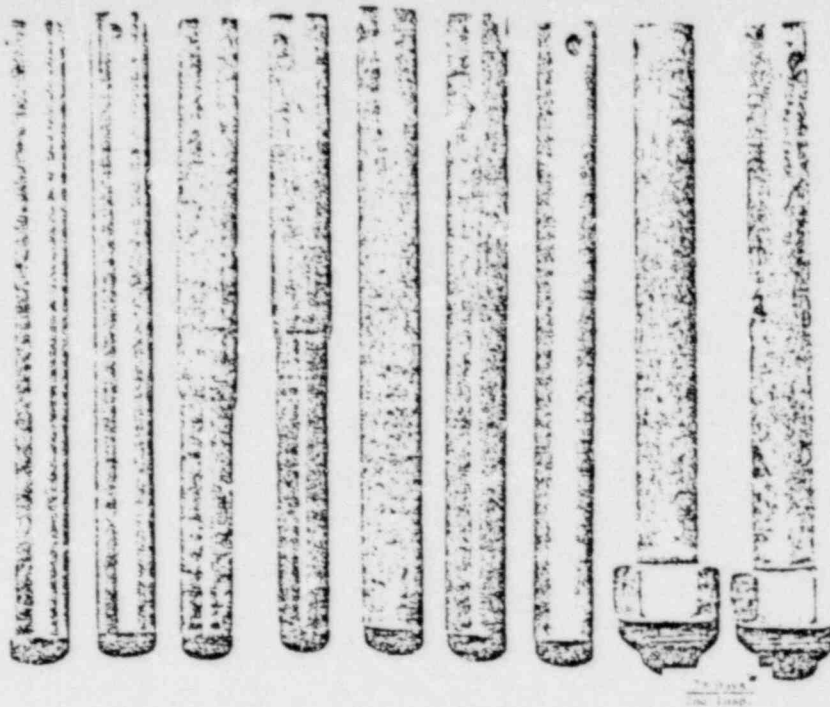


Figure 3

Stress corrosion crack in the 1M1-1 type 304SS spent fuel pool piping. 11 X, nitric etched.



FROM LEFT:

- #1 as-received (sol'n annealed)
- #2 " " " "
- #3 machined, heat treated H-1100
- #4 without degreasing
- #5 heat treated H-1100\* scale intact
- #6 heat treated H-1100\*, lower half pickled 16 hrs. in 20%  $\text{HNO}_3$  to remove scale
- #7 H-1100\* followed by grit blasting
- #8 & 9  
H-1100\* Type 304 with stainless steel not on threaded end

\*H-1100 = 4 hours at  $580^\circ\text{C}$ , air cooled.

Figure 4  
In this figure, the H-1100 specimens after 70 days in the HFBR spent cell  
are shown. The specimens are: #1 - as-received; #2 - sol'n annealed; #3 - machined; #4 - machined, heat treated; #5 - heat treated, scale intact; #6 - heat treated, lower half pickled; #7 - heat treated, grit blasted; #8 & #9 - Type 304 with stainless steel not on threaded end.

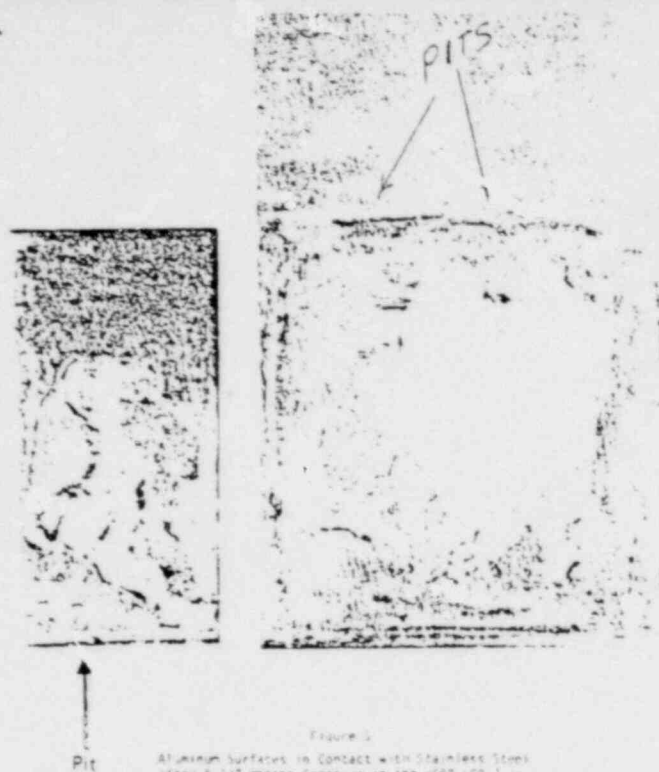


Figure 5  
Aluminum Surfaces in Contact with Stainless Steels  
after 6 1/2 months Exposure in the HSR-VR Loop

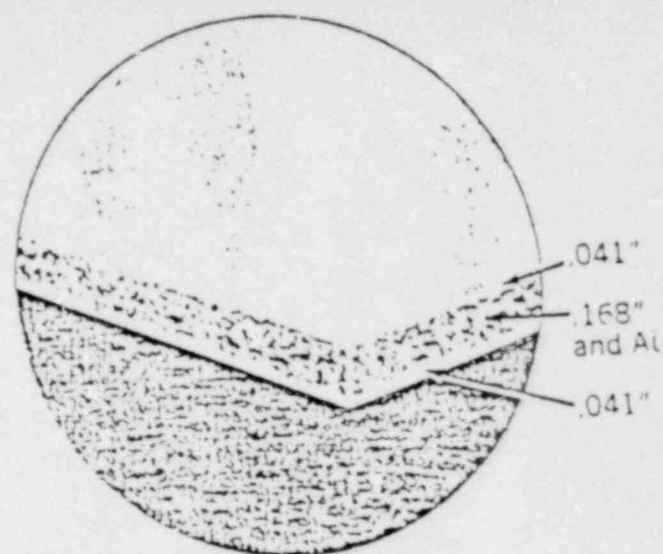


Figure 6  
Typical Cross-section of 1/4" thick Dural.

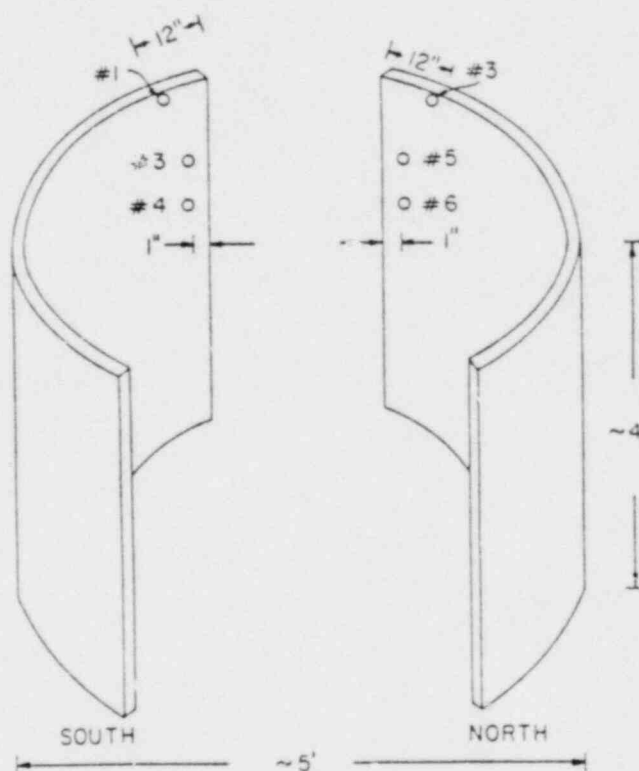


Figure 7  
Schematic of 1/4" Borel Sheets in BWR,  
Indicating Location of Punchings.



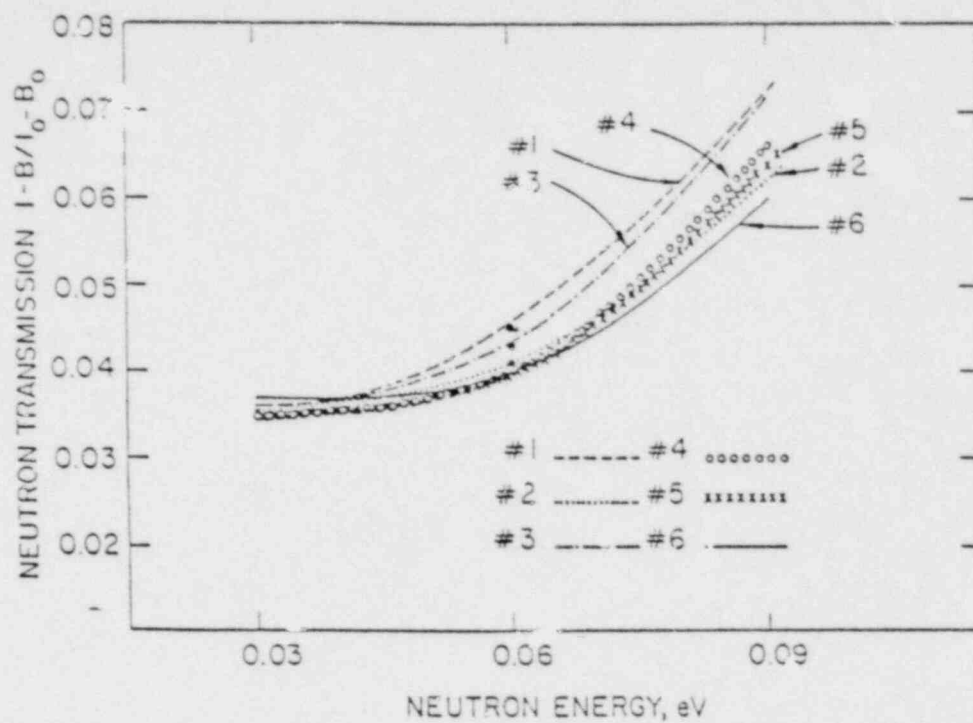


Figure 8  
Neutron Attenuation Results on Samples 1-6 (Performed at U. of Michigan, Courtesy of Brooks & Perkins).

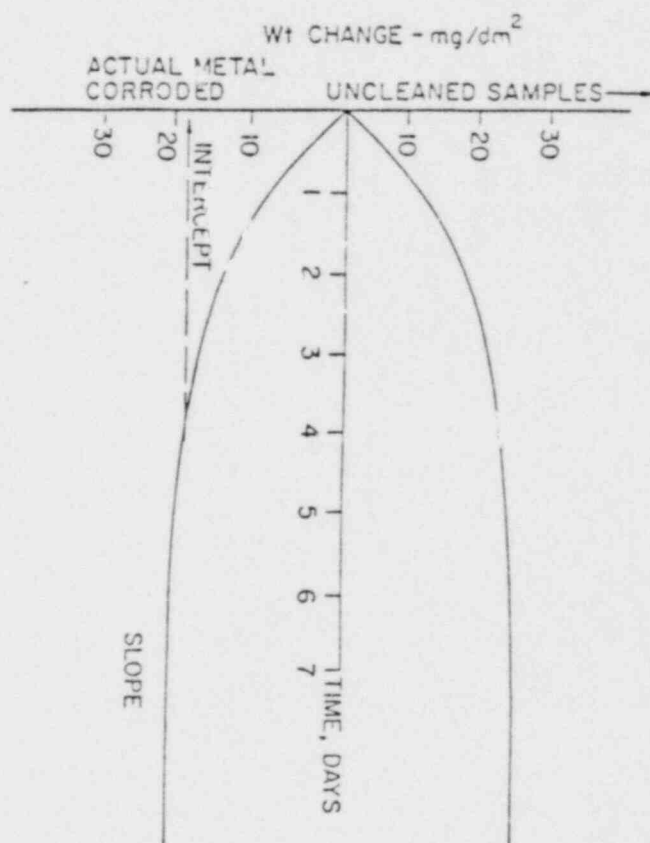


Figure 9  
Typical Corrosion Pattern for 1100 Al in Water  
(from 4NL-5001)