BNL-NUREG -25582
INFORMAL REPORT

CORROSION CONSIDERATIONS
IN THE
USE OF BORAL IN SPENT FUEL STORAGE POOL RACKS

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JANUARY 1979

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Prepared for the U.S. Nuclear Regulatory Commission
Office of Nuclear Reactor Regulation
Contract No. DE-AC02-76CH00016

Dupe of
7905150201

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INTRODUCTION

Boral is a cermet of Boron Carbide "B_4C" in aluminum clad in aluminum. It is manufactured in rolled sheets using techniques similar to those used in the production of uranium aluminum fuel elements. The core of the standard Boral contains 35% boron carbide by weight. Cladding material is typical 1100 aluminum. Where it is exposed to water in service, the edges of the Boral are recommended by the manufacturer to be clad with aluminum by welding.

In Spent Fuel Pool (SFP) racks, the Boral is usually not a structural member but is inserted in cavities between the spent fuel storage positions in the racks. In these locations it is sealed by welding to prevent access of water. Inherently, however, the corrosion of the Boral, both the boron carbide-aluminum cermet and the aluminum cladding, should be minimal in a spent fuel storage pool. The cavities into which the Boral is sealed are typically fabricated of aluminum alloys, i.e. type 6061, or stainless steel. In either case, these are the structural members of the SFP racks.

In an SFP, water chemistry tends to be strictly controlled because the SFP water mixes with the reactor coolant during refueling procedures. In SFP's at BWR sites, water chemistry is typical of that of a BWR i.e. high resistivity neutral water. In SFP's at PWR sites water chemistry typically contains 2 to 3,000 parts per million ppm boron as boric acid, which is there primarily to prevent dilution of the reactor primary coolant during refueling and is not relied on for criticality considerations. The water chemistries and anticipated corrosion of SFP materials were reviewed in an earlier report. BNL-NUREG 23021, July, 1977.

CORROSION OF BORAL

Corrosion problems have developed in SFP's where water has inadvertently leaked into the cavities containing the Boral. In a BWR pool, swelling of the racks has been observed when water leaked into the cavities through a flaw in the seal weld at the bottom of the cavity.

The swelling observed arises from the rapid initial corrosion of Al by water. Draley and Ruther (ANL-5001, Feb. 1, 1953) have shown that aqueous corrosion of 1100 Al can be described in terms of a steady state slope and an intercept, as sketched in Fig. 1. This intercept was measured by them to be 21 ± 5 mg/dm^2 "metal corroded" over a range of temperatures (100 - 175°C) and pH (5 - 8.5). This "intercept" corrosion occurs within the first 5 days of immersion in water by a reaction of the type

$$2Al + (3+x)H_2O \quad Al_2O_3.x\ H_2O + 3H_2.$$

Thus 21 mg Al can produce $\frac{21 X 3}{27 X 2}$, or slightly more than 1 millimole H_2 per dm^2 of surface. The Brooks & Perkins Report #577 says there are 3.4×10^2 dm^2 Boral per tube in SPF racks such as those at Monticello or Brown's Ferry, so one could produce approximately $3.4 X 10^2 x 22.4$ = approximately 7500cc H_2/tube, at STP. This is more than enough to produce the necessary 6 psi to bulge the cladding in a void volume of 130cc.

There is no reason to believe, however, that any B_4C will be lost from the Boral by corrosion in the SFP water. In the Brookhaven

Medical Research Reactor, Boral has been exposed to the reactor coolant since January, 1959. Figure 2 shows a schematic of this reactor. The 1/4 inch Boral sheets are in the form of 2 half-cylinders. The upper edge of these sheets is unclad. The vertical edges appear by examination in situ with a periscope to be clad. In July of this year, samples were removed in the form of small punchings, three from each of the half-cylinders as shown on the attached sketch, figure 3. Each of these six specimens was cut in half, and one-half mounted for metallography. The resultant microstructures are shown in figures 4-9. Clearly there appears to be no systematic loss of the boron carbide. The other half of each of these specimens was analyzed by neutron attenuation at the University of Michigan under contract with Brooks and Perkins, the primary supplier. The neutron attenuation results are shown in figure 10. All the results are within 20%, which with the small size of the specimens is probably within analytical error. One specimen, #5, was analyzed wet chemically by Brooks and Perkins to contain 41.3% B_4C in the core, which is in the upper range of boron concentrations for material produced in the 1950's. It, therefore, seems reasonable to conclude that no boron was lost from the core of this Boral by exposure to the BMRR coolant over the 19 1/2 year period. In the location of the BMRR where it is used, there is little measureable neutron flux. Water chemistry in this reactor is outlined in Table 1.

PITTING OF ALUMINUM IN CONTACT WITH STAINLESS STEEL

When aluminum is contacted with stainless steel in impure water, a potential exists for a galvanic attack of aluminum at the point of contact. In a SFP environment, this attack is especially likely in a PWR pool containing boric acid at a pH around 4.5. Further, aluminum borates can be produced which appear as a white fluffy dispersion in the water at a pH greater than about 4.5. Maintaining the pH below 4.2 causes the white fluffy material to disappear. Corrosion currents at a stainless steel to aluminum galvanic couple in boric acid were measured to average 2 mils per year although the presence of oxygen or hydrogen peroxide increased this value substantially.

A number of references exist showing that pitting corrosion can occur in slightly acid waters at aluminum to stainless steel junctions. English and Griess (ORNL-TM-1030, 1966) report pitting depths up to 45 mils in 12,500 hours (1 1/2 years) in pH 5 nitric acid solutions at 100°C. Lennox et al. (Materials Performance, Vol. 13, #2, page 31, 1974) measured pitting where type 5086 aluminum is coupled to type 304 stainless steel of the order of 30 mils in a year and one-half in Gatun Lake, Panama, and up to 40 mils in two years in the Potomac River at Washington. The general corrosion of this alloy was negligible in both environments.

In the HFBR SFP, water chemistry is similar to that in a BWR SFP except that conductivity may be slightly higher, and the pH slightly lower. Typical data are given in Table 2. Specimens of aluminum and stainless steel in contact with one another have been exposed in the HFBR pool for a period of six months at which time they were examined and then reinserted for continued testing. There appears to be a general discoloration of the aluminum where it contacted the stainless steel and a small amount of pitting around the edges as shown in figure 11. It is highly unlikely, however, that pitting of this magnitude would result in significant loss of the boron should the Boral containing cavities be flooded over an extended period of time.

Venting the upper end of the Boral chambers would probably alleviate any concerns over swelling due to hydrogen generation. It might produce pitting corrosion and some of the white aluminum borate deposits. I would recommend that a surveillance program including aluminum to stainless steel couples be installed in SFP's in which the Boral cavities are vented. Any swelling due to hydrogen production should occur within a week or so of the time the water enters the annulus containing the Boral. However, should a leak develop in one of the seal welds at some future date after the racks are installed, the swelling could occur at that time. For this reason, venting or the capability for future venting, is probably desirable. In general, I think the localized pitting corrosion that might result from venting the Boral cavities in SFP racks would be less of a safety concern than the swelling that might occur should they not be vented. In all SFP's the rack design should prevent contact between Al and the zircaloy fuel cladding, as this galvanic couple (especially in boric acid pools) can lead to hydriding of the zircaloy during storage, as described by A. B. Johnson in BNWL 2256, September, 1977.

CONCLUSIONS AND RECOMMENDATIONS

1. The swelling that has occurred in the Monticello SFP racks and might be anticipated to occur in other similar SFP racks results from initial corrosion of aluminum and not from corrosion of the boron carbide cermet.

2. Venting of these cavities in a BWR pool should not produce significant loss of the boron and should, therefore, be accepted by NRC provided the venting occurs at the upper edge so that any hydrogen pressure from corrosion of the aluminum cladding will not build up to cause swelling of the racks.

3. Venting of the Boral cavities in a PWR rack might produce more pitting corrosion of the Boral. Again, however, it should not lead to major loss of the boron carbide.

4. Anodizing the Boral in these cavities would tend to reduce the hydrogen production in the cavities should SFP water leak in to them. Anodizing would probably not, however, prevent pitting of the aluminum.

5. In any fuel pool in which the Boral cavities are flooded intentionally or inadvertently, surveillance specimens should be present to determine on a periodic basis, i.e. once every few years, what is happening to the Boral in these cavities.

6. In any SFP, galvanic coupling between Al in the racks and the zircaloy fuel cladding should be avoided, to prevent hydriding of the cladding during long term storage.

ACKNOWLEDGEMENTS

The assistance of the BNL Reactor Division staff, R.W. Powell, Head, in obtaining the Boral punchings from the BMRR spent fuel shielding is deeply appreciated. The metallography was performed by K. Sutter of BNL. The neutron attenuation and wet chemistry results were obtained through the courtesy of Mr. R. C. Karzmar of Brooks and Perkins, Inc. More detailed analyses of these specimens are underway at G.E., by A. Jacobs, and at Brooks and Perkins, and will be the subject of a future report.

TABLE I

BMRR WATER CHEMISTRY

Temperature	Inlet	Outlet	T.S.
Reactor ON	100°F	115°F	136°F
Reactor OFF	75-80	75-80	-

(Reactor ON less than 10% of time)

Conductivity	Normal	Regenerate Demineralize	Alarm	T.S.
(μmho/cm @25°C)	<2	2	5	10

Alarmed only once in 20 years, during HX leak. T.S. never exceeded.

TABLE II

HFBR SFP CHEMISTRY

Resistivity meg-ohm-cm	Temp. °C	ppb Cl^-	pH
.24 - .6	30-35	4-20	5.9-7.0

(low pH coincides with low resistivity)

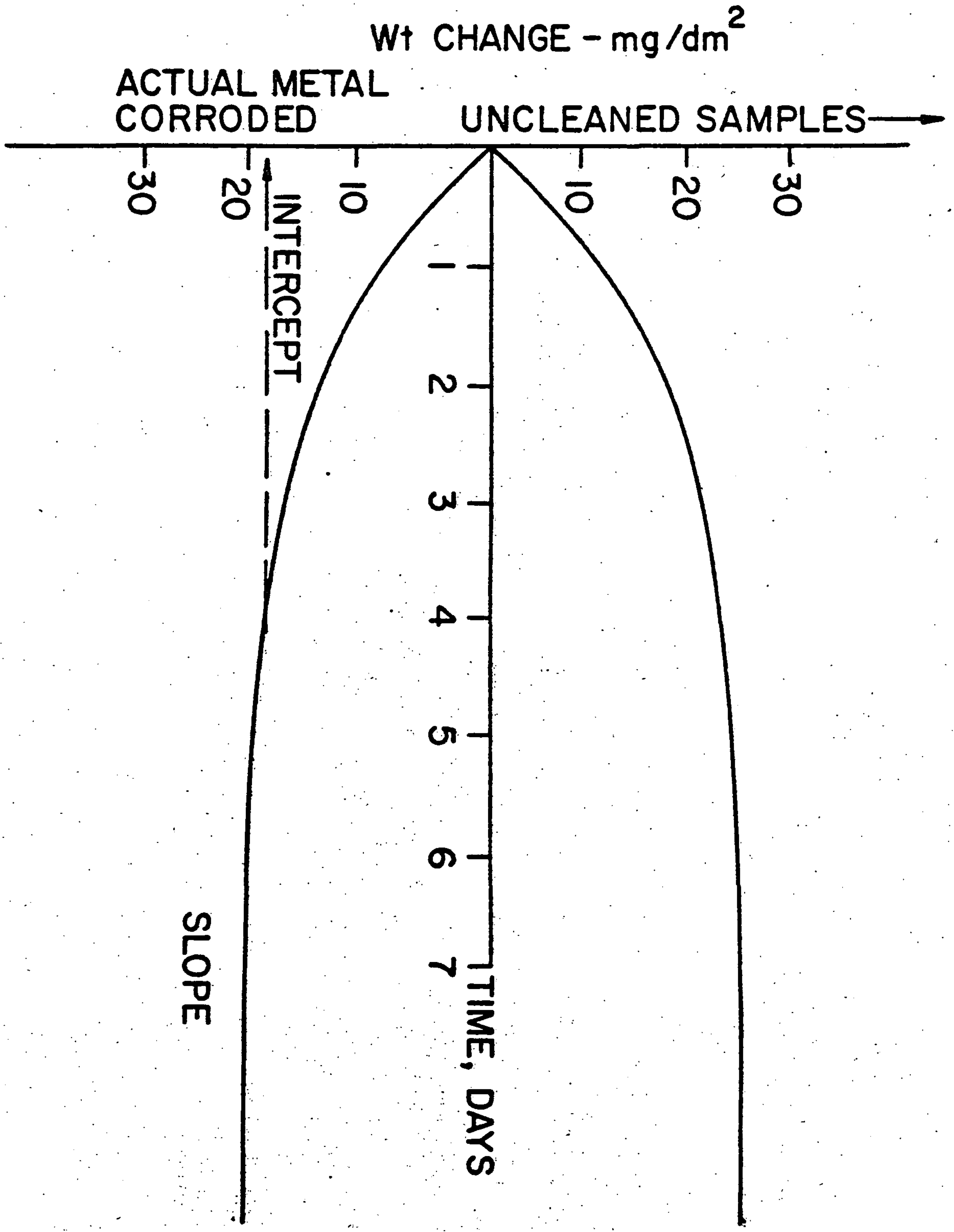


FIG. 1 Typical Corrosion Pattern for 1100 Al in Water (From ANL-5001)

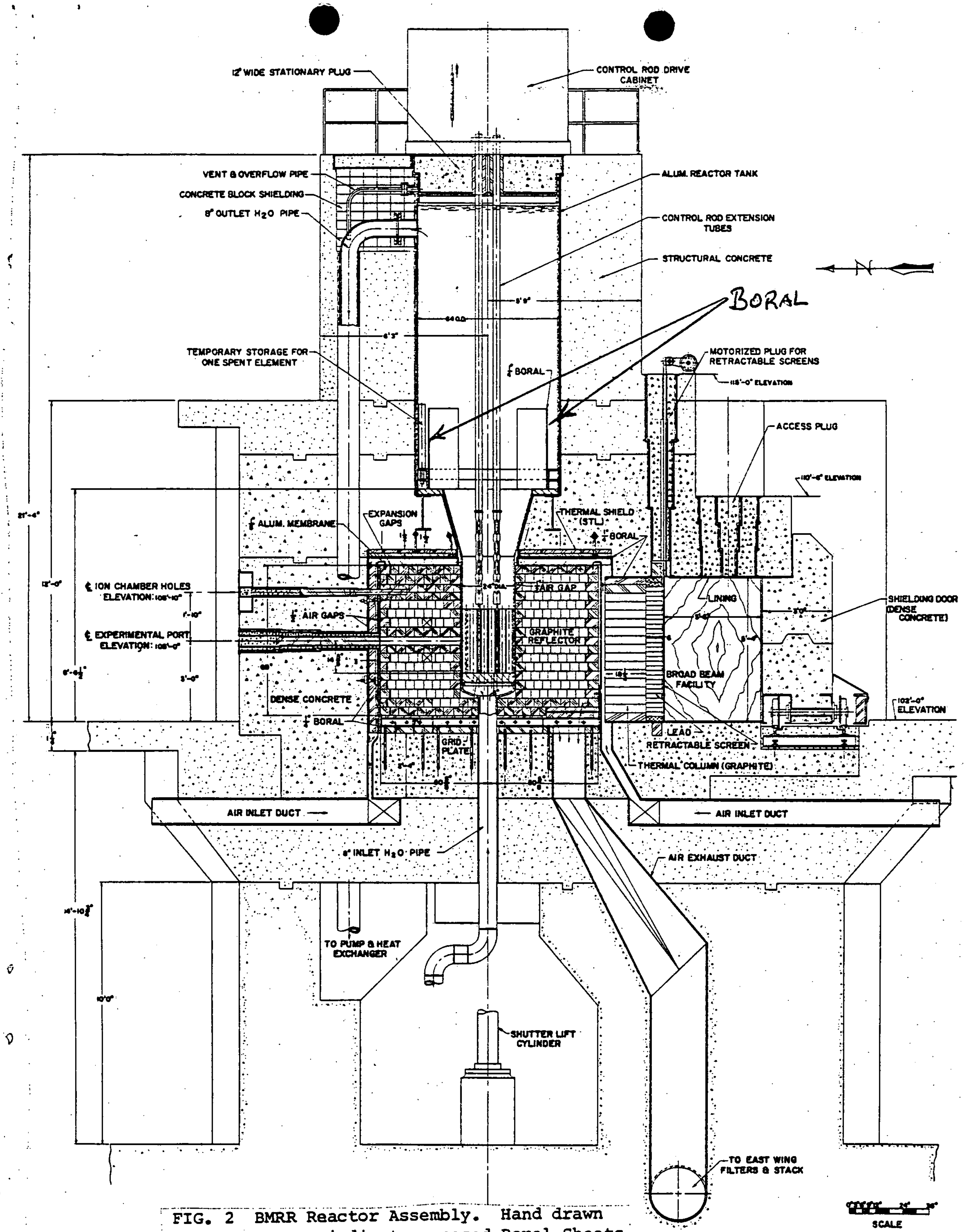


FIG. 2 BMRR Reactor Assembly. Hand drawn arrows indicate exposed Boral Sheets. From BNL-600.

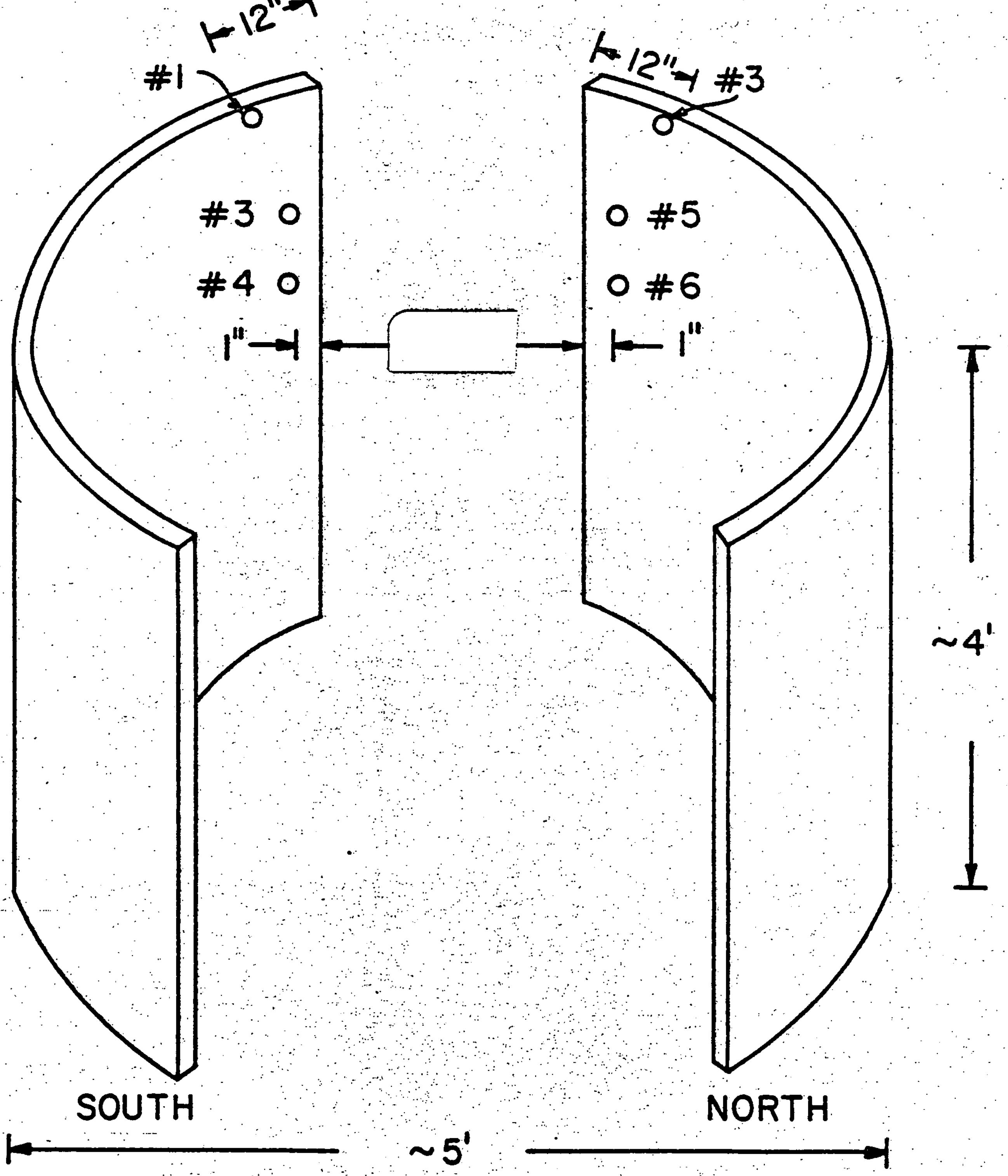
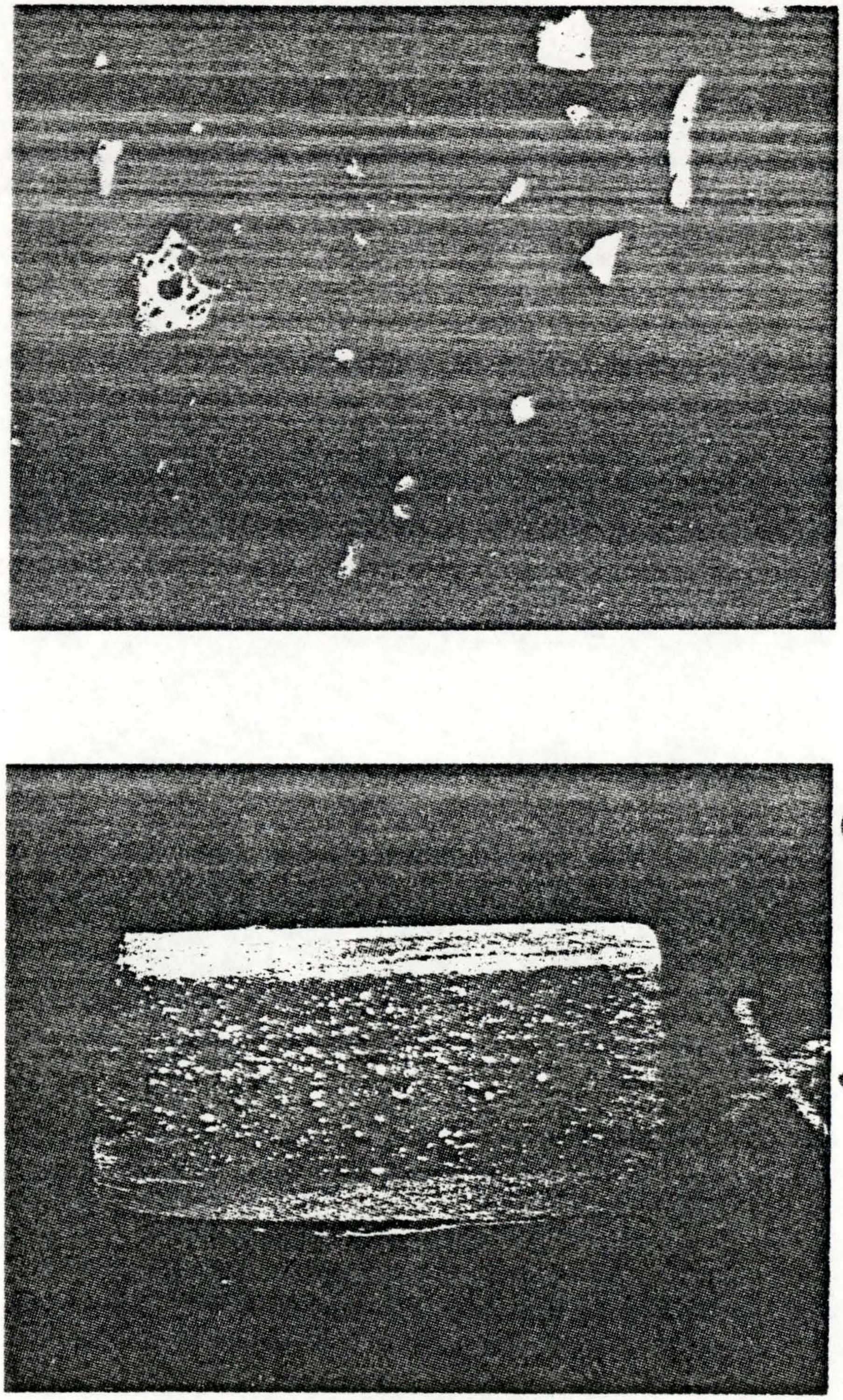


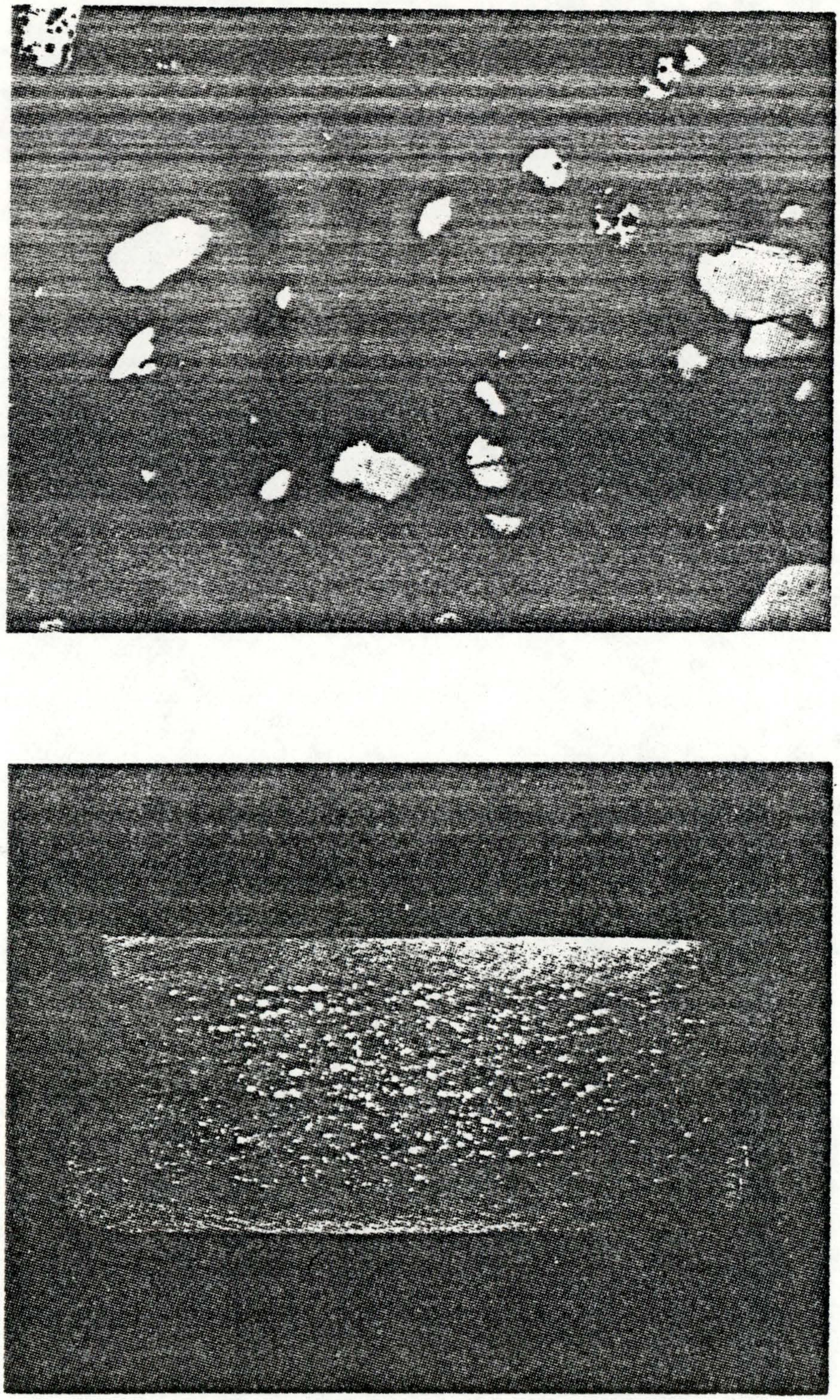
FIG. 3 Schematic of 1/4" Boral Sheets in BMRR, Indicating Location of Punchings



X7 Sample #1 X100

↑ Exposed end

FIG. 4



X7

Sample # 2

X100

FIG. 5

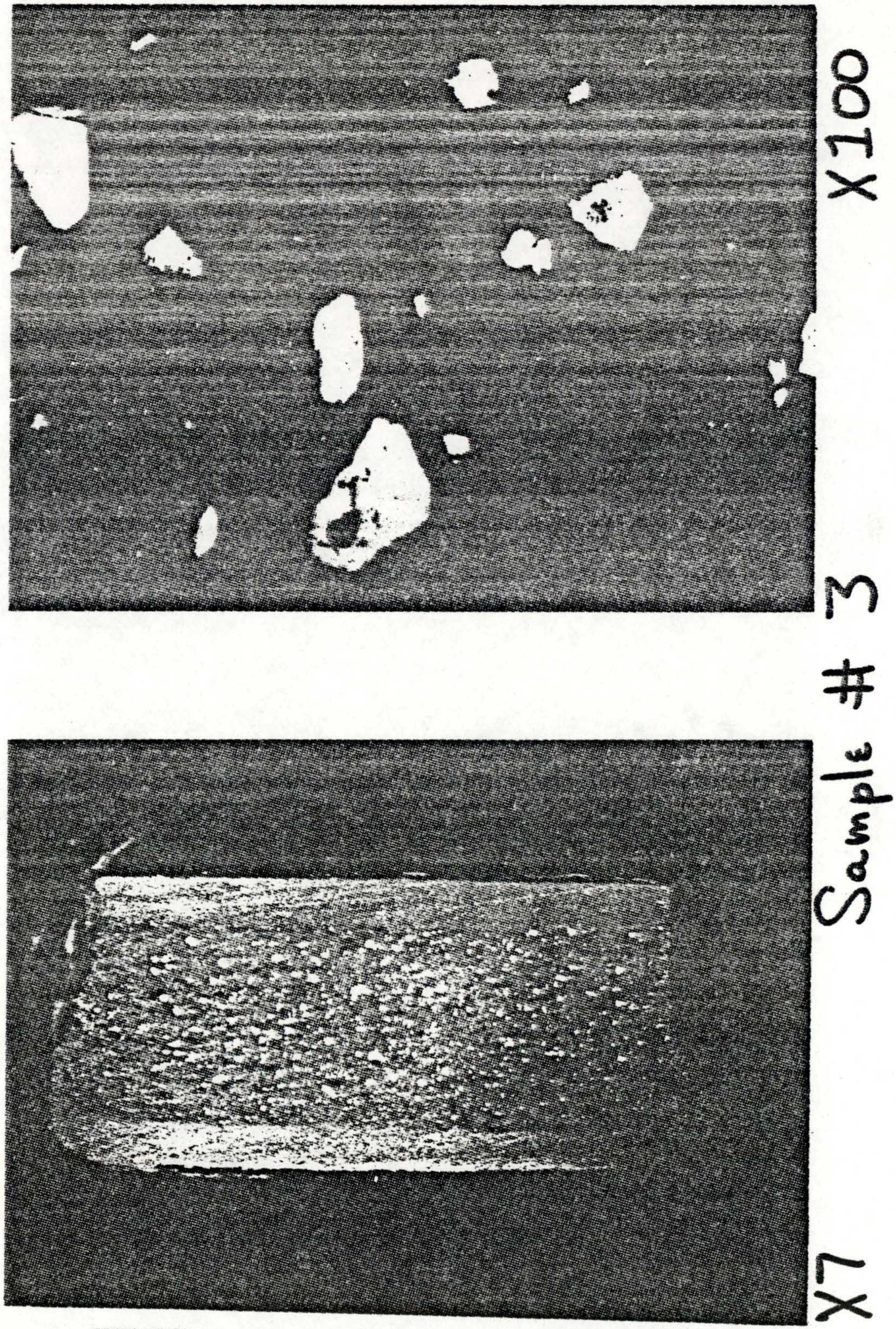
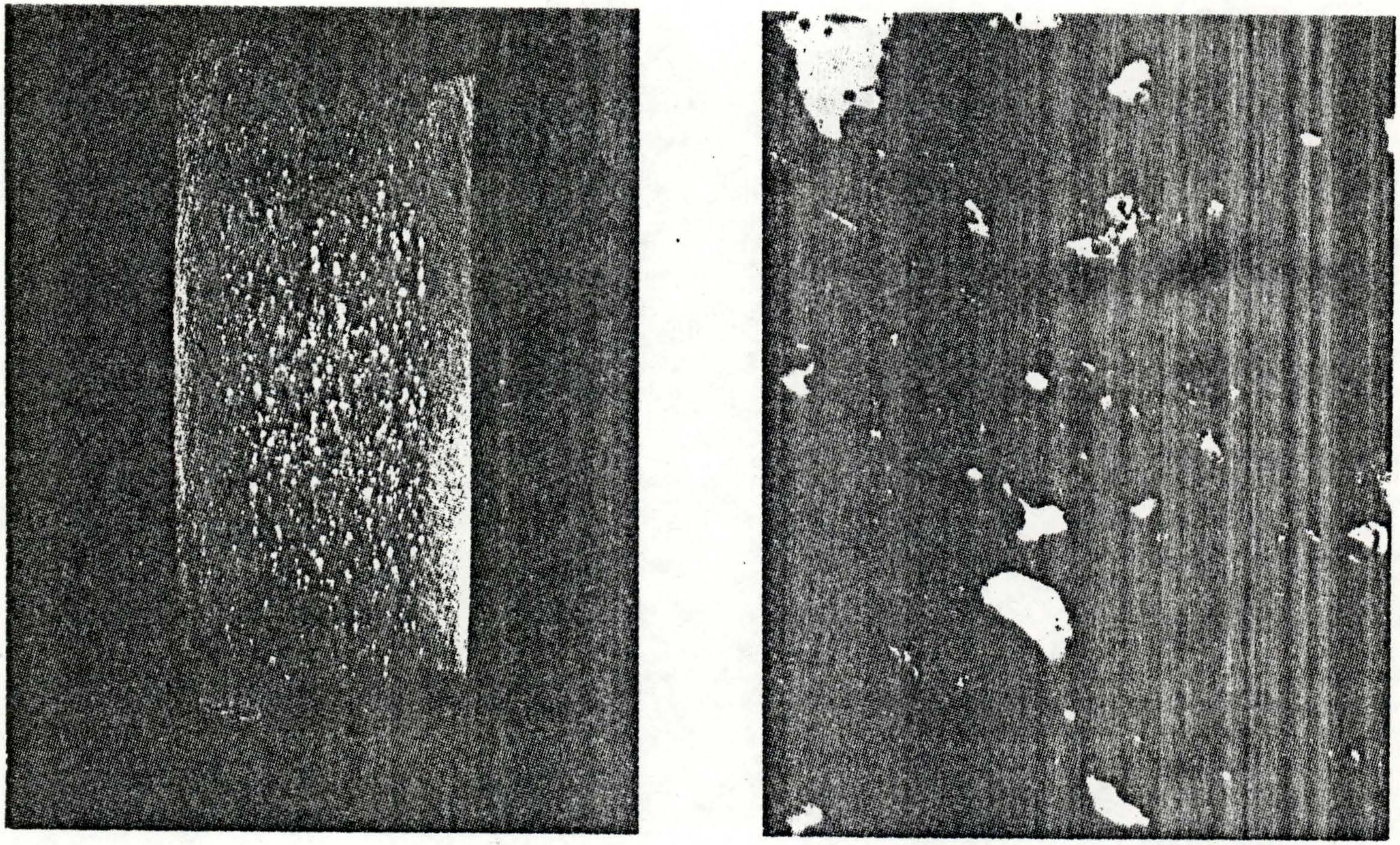


FIG. 6

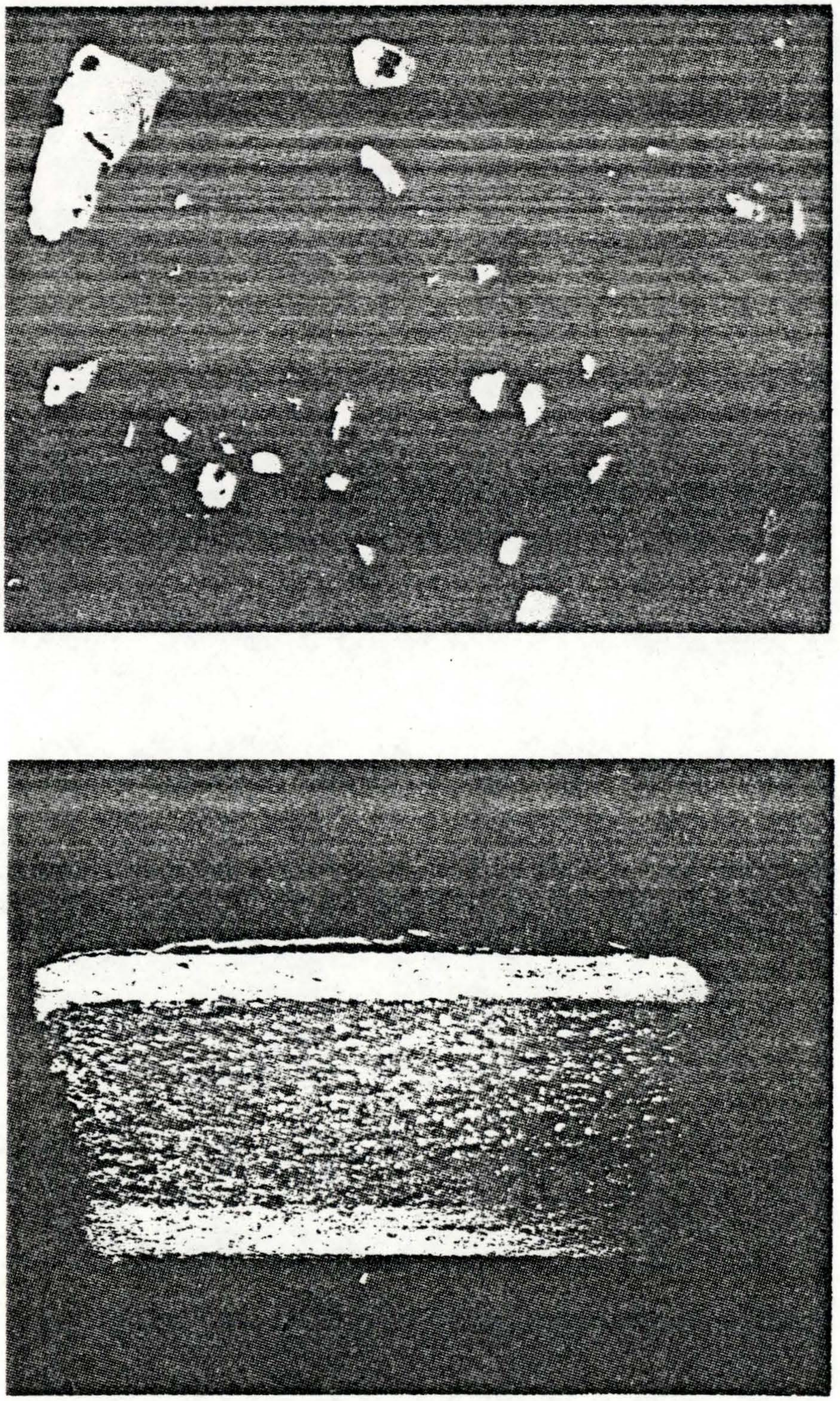
FIG. 7



X7

Sample # 4

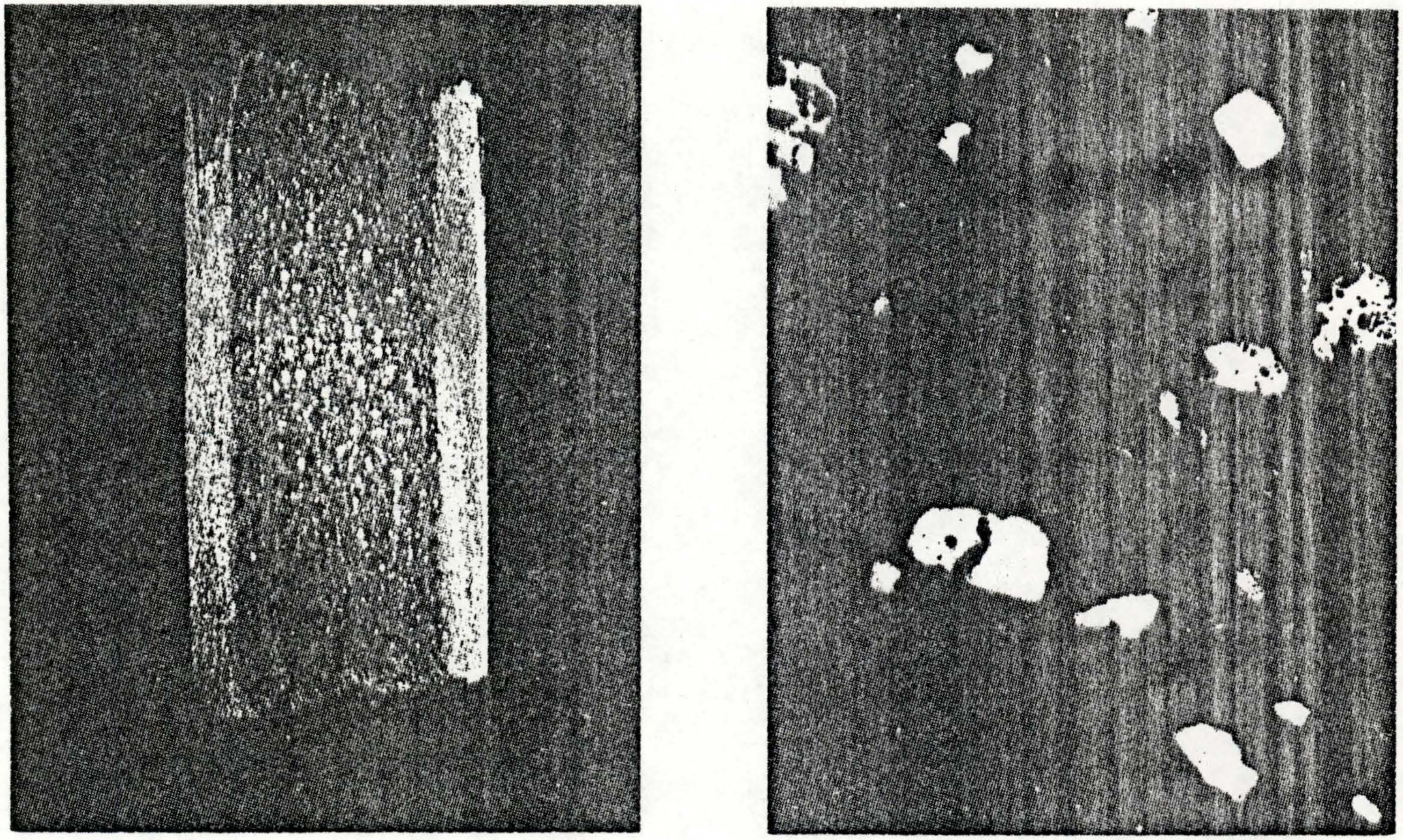
X100



X7 Sample #5 X100

FIG. 8

FIG. 9



X7 Sample # 6 X100

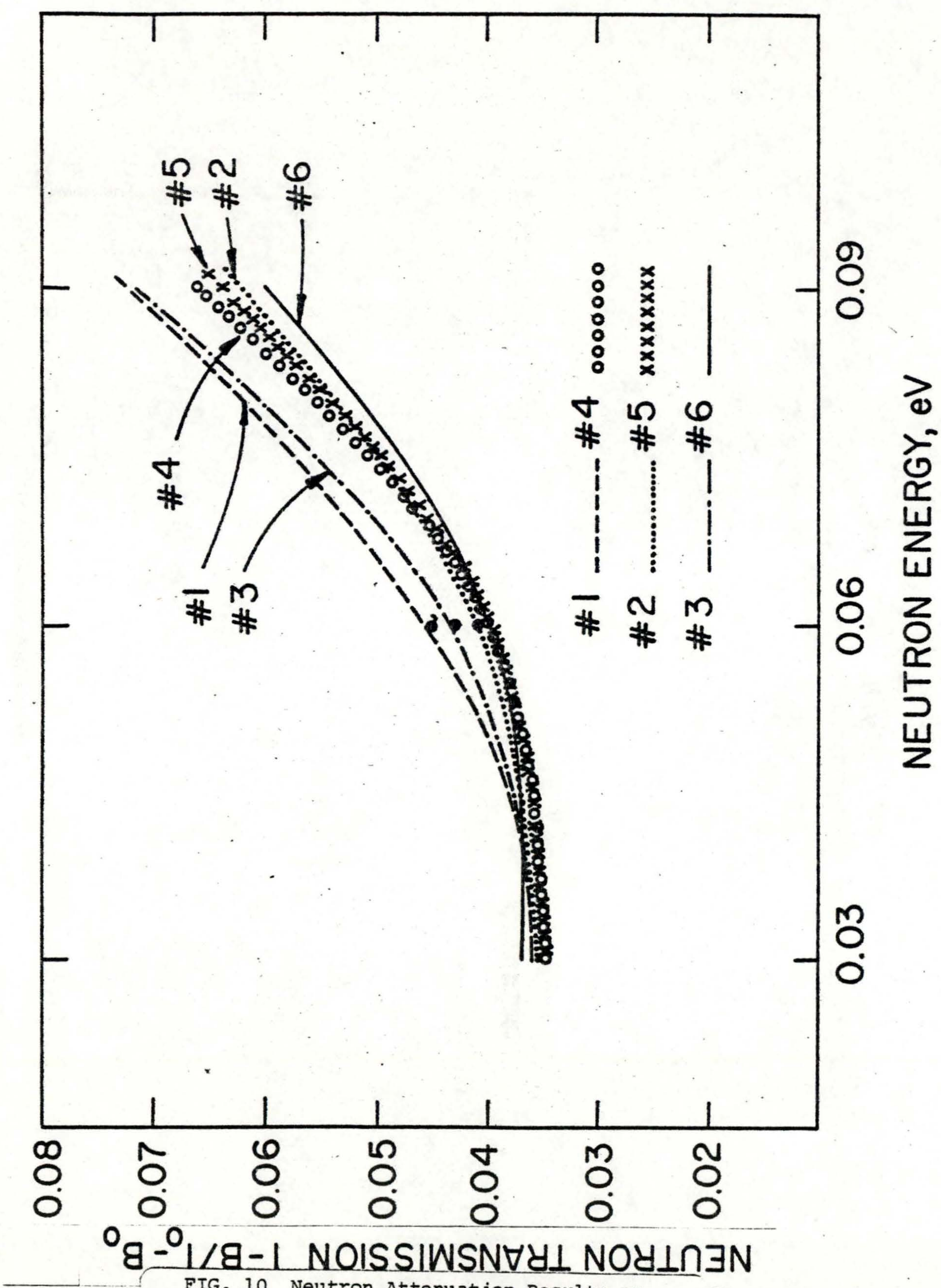


FIG. 10 Neutron Attenuation Results on Samples 1-6 (Performed at U. of Michigan, Courtesy of Brooks & Perkins

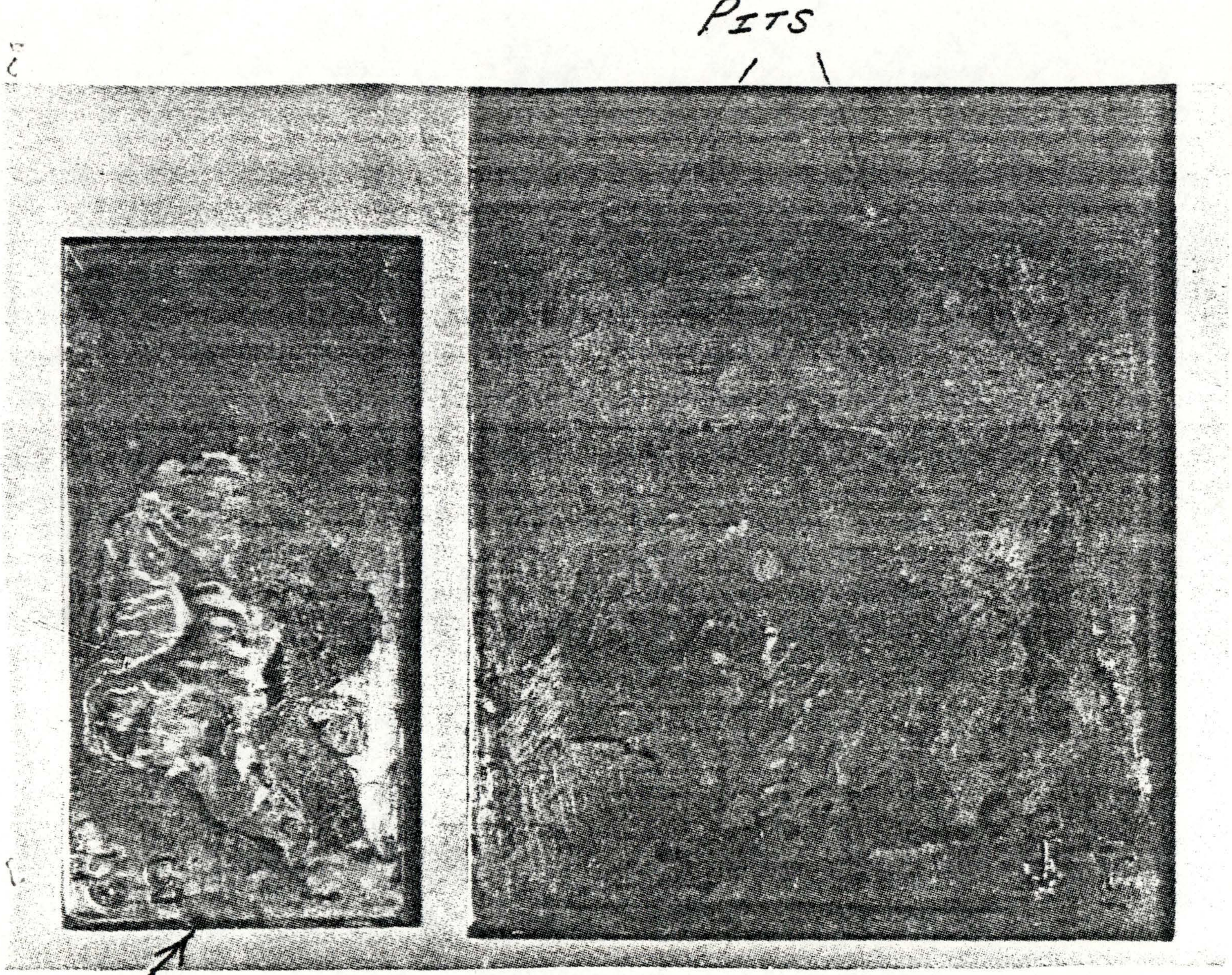


FIG. 11 Aluminum Surfaces in Contact with Stainless Steel after 6 1/2 months Exposure in the HFBR SFP 2.5x

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