February 11, 1987

RESULTS OF BORAFLEX EXAMINATION
POINT BEACH NUCLEAR PLANT

Background

Our license amendment application to increase the spent fuel storage capacity at Point Beach Nuclear Plant (PBNP) was submitted to NRC on March 21, 1978. In response to NRC requests for additional information, we described a surveillance program to verify the continued integrity of the Boraflex material contained in the spent fuel storage racks. This program utilized 30 standard, 2" x 2" Boraflex squares per pool that were control checked and placed in a surveillance train (See Figure 1). These samples were then suspended in a poison box location in the spent fuel pool (SFP) such that freshly discharged spent fuel assemblies could be placed next to the surveillance sample location, thus providing maximum irradiation to the samples. Tests were to be performed after two years exposure, five years exposure, and ten years exposure. Additional testing or changes to the frequency of testing could be specified, depending upon the evaluation of specimens removed during the early portion of the program.

BISCO Report No. 1047-1, "Boraflex I Suitability Report", Revision 1, dated May 5, 1978 provides information on the testing done to qualify Boraflex for use in the radiation and borated water environment found in the SFP. In these tests, Boraflex was irradiated to integrated gamma doses of approximately 10^8 and 10^9 rads. At these dose levels, testing was done to measure changes in tensile strength, elongation, elastic modulus, dimensions, weight, and hardness. Additionally, a study of gases evolved in the test chamber was conducted. The qualification study also immersed Boraflex in 3,000 ppm borated water for a period in excess of 4,700 hours. The water temperature was 240°F, and the water pH was adjusted by the addition of NaOH to a range of 9.0 to 9.5.

In BISCO Report No. 748-10-1, "Irradiation Study of Boraflex Neutron Shielding Materials", dated July 25, 1979, the test program further checked the stability of the Boraflex and the neutron attenuation capability of the boraflex at a cummulative gamma level of 10^{11} rads.

The qualification studies generally indicated Boraflex to be stable in the high temperature, water soak, and radiation environment found in a spent fuel pool. The data indicated that Boraflex will generate gas up to irradiation levels of 1×10^{10} rads gamma. The qualification data indicated that although the Boraflex embrittles with irradiation, there is little loss of neutron absorption properties or redistribution of boron.

Boraflex Use in Point Beach Spent Fuel Racks

Boraflex was chosen for use as the neutron poison material in the Point Beach spent fuel racks with a recognition of its limitations. For example, because Boraflex becomes embrittled and experiences some dimensional decrease due to gamma radiation, bonding of Boraflex in the spent fuel racks was eliminated from the Point Beach design and assembly procedure. Instead, the

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the Boraflex sheet was simply placed within stainless steel clad that essentially forms a complete envelope around the Boraflex. This arrangement also eliminates any loading to be transmitted to the Boraflex. To prevent poison assembly swelling due to offgassing, the tight-fitting stainless steel envelope was also vented at the top and made open to the SFP water environment.

Elimination of the potential for galvanic corrosion was an important consideration in the selection of Boraflex over alternative metallic or metal-containing materials.

The sample test program has confirmed some of the known limitations, but the overall behavior of Boraflex in the racks is within expectations. Nevertheless, in the Point Beach spent fuel rack design, the poison inserts are individually replaceable should long-term neutron attentuation degradation develop in the Boraflex.

<u>Surveillance Specimen Program - March 1985 Testing and Results</u>

In accordance with the Point Beach Nuclear Plant Boraflex sample surveillance program, six Boraflex specimens (North Pool - N7, N8, & N9; South Pool - S4, S5, & S6) were cut from their respective sample trains and shipped to the Georgia Institute of Technology in March of 1985 for testing. This testing program included neutron radiography of the samples, neutron attenuation testing utilizing a thermal beam of neutrons at an energy of .037 eV, weight and thickness measurements, hardness testing in a Shore A durometer, and isotopic analysis of the boraflex.

The specimens were dried out in an attempt to decontaminate and reduce the radiation levels of the specimens prior to shipment to Georgia Tech. Contact radiation readings of the samples at PBNP averaged 35-45 mRad beta-gamma per hour. Subsequent isotopic analysis of the samples at Georgia Tech determined that these radiation levels resulted principally from Cobalt-60, Cesium-134, and Silver-110. In effect, the Boraflex samples had acted as a sponge and had absorbed some spent fuel pool water.

In packaging for shipment, the Boraflex samples were retained inside the original clad channels that were cut from the sample trains. The stainless steel clad was then inserted in a snug fit between lead shielding designed for a 2-2.5 inch pipe. This was then banded, wrapped, and placed in a 55 gallon shipping drum. When the drum was opened at Georgia Tech, it was observed that the stainless clad had bent somewhat and was applying a slight force to the Boraflex samples contained therein. This torsion may have contributed to some breakage of the already brittle samples.

At Georgia Tech the Boraflex specimens were observed to have broken into multiple smaller chips. These chips were friable with a small amount of graphite-like particulate matter loosely covering them. The Boraflex chips were large enough to obtain neutron attenuation data, hardness data, and some of the thickness data requested in the test program. However, width and weight measurements could not be obtained as specified in the test program due to the crumbled state of the specimens.

Hardness of the specimens in the Shore A durometer was 100 or fully hard. This is higher than the original material qualification studies projected. Neutron attenuation capability of the Boraflex was about 99%, slightly higher than projected. Sample thickness averaged about 0.1 inch and had decreased roughly as the qualification studies projected. No conclusions could be drawn concerning the change in weight and width of the specimens due to their broken state. The total gamma dose to the north and south trains was estimated at 1.4×10^{10} R and 1.0×10^{10} R, respectively.

In reviewing the specimen degradation problems, several factors, alone or in combination, were thought to have contributed:

- The specimens were thoroughly dried out prior to shipping.
- Shipping and handling, although accomplished carefully, did apply some torsion and shocks to the specimens.
- The PBNP Boraflex specimens may have been exposed to an environment outside of BISCO's original material qualification envelope. In other words, the Boraflex immersion tests in BISCO's qualification study were done in a borated solution of 3,000 parts per million boron in the form of boric acid that was, however, pH adjusted by the addition of sodium hydroxide to a pH range of 9.0 to 9.5. This differs from the Point Beach SFP environment in which the pH ranges from 4.5 to 4.9. See Attachment 1 for typical chemistry in the Point Beach SFP.

As initial resolution of the problems of specimen degradation and ensuing testing, several actions were taken.

- Point Beach, Reactor Engineering Instruction REI-25, "Spent Fuel Rack Neutron Absorbing Material Surveillance Specimen Program," was revised to test additional Boraflex specimens immediately and in mid-1987. This was in addition to the testing scheduled for 1990, the ten-year test date.
- In preparing the Boraflex samples for shipment, they would be braced and shipped in a moist condition, with no loose water in the shipping package.
- Chemical analysis would be included in future Boraflex testing to determine if the Boraflex may be undergoing a chemical reaction in the SFP environment.

Also at this time, the geometry of poison inserts and lead-in guides in the spent fuel racks was carefully reviewed. It was determined that the nominally 0.11 inch thick Boraflex sheets were closely retained by the clad such that "slumping" of the Boraflex material could not occur even if it should crack. The Boraflex material is sandwiched between two pieces of stainless steel sheet that are completely seam-welded on three sides and seam-welded on the top with intermittent fusion to allow gases to escape.

Supplemental Surveillance - October 1985 Testing and Results

In October of 1985, three more boraflex samples (N10, N11, & N12) were shipped to Georgia Tech for a similar testing program. The total gamma dose received by the test samples was 1.6×10^{10} rads. The samples were shipped to Georgia Tech in a container of SFP water that was further packed in a shipping drum. Upon unpacking the samples at Georgia Tech, it was observed that the water used to ship the samples was black.

Subsequent inspection and testing of the samples revealed that the corners of the Boraflex samples were rounded and the edges were eroded. In fact, sample thickness, width, and weight for these samples decreased an average of 30%, 15%, and 50%, respectively. Neutron attenuation capability of the Boraflex samples, however, was approximately 95% and within qualification projections. Hardness measurements in the Shore A durometer indicated one sample to be 100 and the other two only slightly less. Chemical composition testing (spectographic analysis and gas chromatograph mass spectroscopy) on a Boraflex sample and the surrounding graphite-like powder had been specified but could not be performed due to the contamination level of the samples.

While the water in the shipping container was black with graphite-like particulate shed from the samples, the Boraflex color itself was gray. Successive immersions of the Boraflex sample into beakers of clear water darkened the water, but each time to a lesser extent. The Boraflex sample, in turn, lightened to a whitish gray. When a sample of this rinsed Boraflex was placed in a beaker and magnetically stirred for 36 hours, the water stayed clear and only "crumbs" from the sample came off. No additional "sooty" black material appeared. It should be noted that the graphite-like particulate material shed from the Boraflex did not appear to dissolve to any extent, but eventually settled to the bottom of the beakers.

Again, transportation was suspected as having caused degradation of the boraflex samples. It was hypothesized that agitation of the Boraflex container during shipping caused erosion and wear on the Boraflex, much like might occur in a moving stream.

Supplemental Surveillance - April 1986 Testing and Results

To further investigate sample thinning and degradation, an additional sample, N-13, was removed from the SFP in April 1986 and examined at PBNP. Again, the decrease in sample thickness, width, and weight was 27%, 15%, and 50%, respectively. The N-13 data indicated that sample thinning was occurring in the SFP environment and was not resulting primarily from transportation as suspected previously.

In summary, the neutron attenuating capability of the Boraflex was confirmed by the recent testing, but the Boraflex samples were found to be fragile and easily broken. The following summarizes the doses the samples received:

	Gamma Dose
Boraflex Test Samples: N-7, 8, & 9	$\sim 1.44 \times 10^{10}$ rads
S-4, 5, & 6	$\sim 1.0 \times 10^{10}$ rads
(Tested at Georgia Tech in March 1985)	
Boraflex Test Samples: N-10, 11 & 12 (Tested at Georgia Tech in November 1985)	$\sim 1.55 \times 10^{10}$ rads
Boraflex Test Sample: N-13 (Examined at PBNP in April 1986)	$\sim 1.6 \times 10^{10}$ rads

Full-length Boraflex Sheet Examination - August 1986

Since there are significant differences in the geometry and encapsulation

methods between the Boraflex samples and the actual full-length sheets in the spent fuel storage racks, we decided to remove two full-length Boraflex sheets from the SFP and examine them on-site.

On August 18-20, 1986 two Boraflex poison insert and lead-in guide assemblies were removed from the SFP at PBNP and examined. After each assembly was removed from the spent fuel storage racks, a replacement poison assembly, manufactured to original material and dimensional specifications, was immediately installed. The poison inserts were chosen for examination based on the gamma exposure received. One poison insert was highly irradiated; the other was not. This combination was intended to identify whether the SFP water was affecting the Boraflex, apart from known radiation embrittlement. The location of these poison inserts in the SFP and their exposures were as follows:

SFP LOCATION	Gamma Dose
SX-47 (West) -	0 rads
SP-40/41	$\sim 1 \times 10^{10}$ rads
Typical Boraflex insert in spent fuel racks after 40 Years	$1.8\text{-}2.0 \times 10^{10}$ rads

The projected 40 year exposure is based on placing fresh spent fuel in a typical location in the spent fuel racks three (3) times on thirteen (13) year cycles. Hence, the recently tested samples had exposures approaching the 40 year design exposure of the Boraflex in the spent fuel racks. The poison insert from SP-40/41 received one-half of this design exposure, or in other words, an equivalent dose equal to 20 years. The Boraflex insert in position SP-40/41 received accelerated exposure, since it was adjacent to the location of the surveillance test samples, which had recently discharged spent fuel assemblies placed next to them every six months. This compares to a poison insert in the average spent fuel rack position which has received about six (6) years exposure or about 3.0×10^9 rads gamma.

Removal/replacement of the Boraflex insert and lead-in guide assemblies in SFP positions SX-47 and SP-40/41 was performed according to Point Beach Nuclear Plant Special Maintenance Procedure (SMP) - 728, "Examination of Boraflex Sheets from Poison Insert Assemblies Removed from the Spent Fuel Racks."

This procedure required immediate replacement with a poison assembly manufactured to the original material specifications after each poison insert was removed from the spent fuel storage racks.

The full length poison inserts selected for examination were chosen to contrast the effect of gamma irradiation and compare the effects of exposure to the SFP water environment on Boraflex. This cause and effect approach was adopted because the original Boraflex material qualification studies were performed by BISCO at a pH level different than that of the Point Beach SFP. In addition, the actual 5-year exposure time to the SFP water environment is more lengthy than that of the qualification testing.

The Boraflex inserts were inspected according to Table 1 - Boraflex Qualitative Inspection Criteria and Table 2 - Boraflex Quantitative Inspection Criteria of SMP-728. These tables are provided in Attachment 2. Attach-

ment 3 is a radiological survey of the samples taken from both of the larger Boraflex sheets. Attachment 4 consists of pictures taken to document the examination of the larger Boraflex sheets.

It should be noted that both Boraflex sheets were wholly intact when initially examined. During the exam, the Boraflex was broken in many places to gauge its brittleness and hardness. The photographs of Attachment 4 document this examination and corresponding cleavage fractures, not the as-found state of the Boraflex.

The poison insert at SX-47 received a negligible gamma dose as spent fuel was not placed in this position. This assembly was selected to see if the acidic environment of the spent fuel pool water was causing the degradation observed in the surveillance specimens. In the absence of gamma radiation, this did not appear to be the case. The poison insert appeared to look brand new. Only a whitish powder covering the Boraflex where it was in contact with the stainless steel clad distinguished the SX-47 Boraflex insert from new Boraflex.

The poison insert at SP-40/41 received accelerated irradiation to 1×10^{10} rads gamma. This insert had good integrity with no pieces missing, no cracking, or other degradation observed. This is unlike the samples S4, 5, and 6 at the same dose. The thickness of the Boraflex sheet was consistent over its length, nominally 0.1 inches. Over most of the insert length, the Boraflex sheet was black and did not have dust or powder being shed from it.

There were some discolored areas along the edges of the Boraflex insert from SP-40/41. These appeared as gray scallops working into the material and typically measured 0.25 inches deep by about 2.5 inches long. The largest gray patch observed was 0.5-0.75 inches deep by about 5 inches long. The gray discolorations were spaced randomly along the edges and probably occupied about 1-2% of the entire Boraflex sheet surface area. These gray areas when first observed were reminiscent of the color of the Boraflex samples. Further examination showed that, although the thickness of the Boraflex at the gray areas was consistent with nominal Boraflex thickness, the gray area yielded a dust or powder much like the samples when rubbed. Overall, the insert from position SP-40/41, although brittle, had good integrity with minimal degradation.

Some additional observations on the full-length Boraflex inserts based on their radiation levels can be made. As stated previously, the Boraflex samples sent to Georgia Tech averaged 35-45 mRad/hour beta-gamma, on contact. These radiation levels were found to principally result from absorption of spent fuel water that contained cobalt and cesium.

The radiation levels of samples taken from the unirradiated Boraflex insert from position SX-47 were less than 2 mRad/hour beta-gamma. This indicates the unirradiated insert hardly absorbed any spent fuel pool water.

The radiation levels of samples taken from the irradiated insert from position SP-40/41 were approximately 2 mRad/hour gamma and 8-12 mRad/hour beta, on contact. These radiation levels are less than the surveillance samples, but still indicate some absorption of spent fuel pool water.

Radiation levels on contact with the discolored, "gray" area from a section of the SP-40/41 insert were approximately 2 mRad/hour gamma, 80-90 mRad/hour beta, and some detectable alpha. This perhaps indicates that spent fuel pool water was being absorbed preferentially along the edges of the Boraflex. It also leads to the following observations about the progression of degradation in the Boraflex:

1. In the absence of gamma radiation, Boraflex appears to be inert to the SFP environment. The unirradiated insert retained "like-new" Boraflex material properties and did not appear to absorb SFP water.

2. With gamma irradiation, the Boraflex polymers appear to change in a manner that allows SFP water to permeate the Boraflex along the edges. When the SFP water does penetrate the Boraflex, the material changes character. It changes a material of good integrity and retention to one that is friable and yields a particulate-like powder. It also changes color from black to gray. Once it has reached the "gray" state, thinning, weight loss, and general degradation appear to follow.

3. It appears SFP water preferentially permeates the Boraflex on the edges where it was cut to a dimension apropriate for placement in the insert assembly. The "finished" broad surface of the Boraflex appears to be resistant to water permeation.

   The 2" x 2" samples in the surveillance program had relatively small distances between cut edges, hence the SFP water could totally saturate the sample in a short period. Also, it would appear that the higher gamma radiation levels received by the samples may have enhanced this process.

4. In the case of Boraflex exposed to PBNP conditions, it appears that Boraflex may begin to be susceptible to water permeation and subsequent changes in material integrity at about 1×10^{10} rads gamma.

Conclusions

The Boraflex samples appear to have experienced more degradation for a given gamma dose than the full length boraflex insert. This degradation only occurs in the presence of gamma irradiation. It is possibly enhanced by differences in the method of encapsulation. Sample degradation may be enhanced due to the fact that the edge area/surface area ratio of the samples is larger than that of actual full sheets. This allows permeation of the SFP water throughout the sample relatively quickly. In contrast, permeation is only evident at the edges of the larger irradiated Boraflex insert. In either case, however, when SFP water permeation occurs the Boraflex material changes from a material of good integrity to one that is easily degraded. The onset of permeation and subsequent Boraflex degradation occurs roughly at 1×10^{10} rads gamma or at the 20 year point in the Boraflex design life at Point Beach. It is believed that the chemical changes described are a second stage degradation mechanism separate from the shrinkage and embrittlement which occur initially in Boraflex in service.

Currently, the average spent fuel pool rack position has accumulated a gamma dose, equivalent to six (6) years exposure of 3.0×10^{9} rads gamma. It is observed that a full length Boraflex insert has good overall integrity through 20 equivalent years or 1×10^{10} rads gamma. Thus, the Boraflex inserts in the racks are expected to retain their serviceability for another 10-20 years.

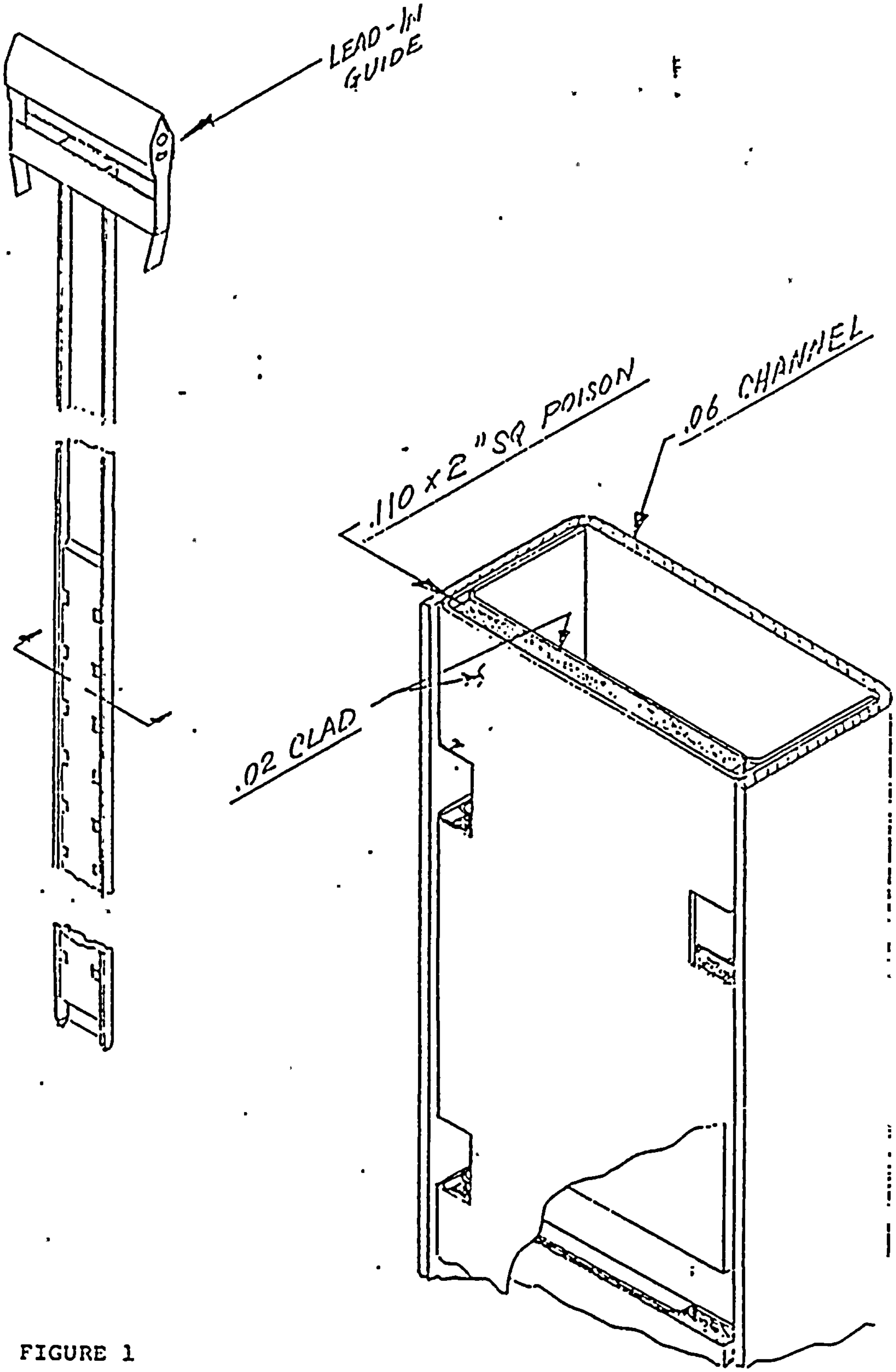


FIGURE 1

ATTACHMENT 1

TYPICAL CHEMISTRY

Parameter	Range
pH	4.5 - 4.8
Cl	<.05 ppm
Fl	<.05 ppm
Boron	~2000 ppm (TS Lower Limit - 1800 ppm)
O_2	4-5 ppm
Si	~5 ppm
Gross B-γ	8×10^{-4} μC/cc

Temperature of the SFP water is controlled between 70°F and 90°F, and it typically runs in the eighties (80's) high in the SFP. At the lower levels in the vicinity of the fuel, temperatures are considerably hotter.

ATTACHMENT 2

TABLE 1

BORAFLEX QUANTITATIVE INSPECTION CRITERIA

Poison insert and lead-in guide assembly:

SFP Location SP-40/41

Total Gamma Dose 1×10^{10} Rads Gamma

Average Values of		Location Along Length of Boraflex Sheet: Top	Middle	Bottom
1. Thickness @ center (inches) (nom. = 0.11")		.095	.101	.096
2. Thickness @ edges (inches)		.094	.111	.102
3. Width (inches) (nom. = 8.0")		7.75	7.75	7.75
4. Weight: IDEAL vs ACTUAL (gms)	Ideal	17.9	17.7	17.2
(Assume $\rho_{boraflex}$ = 1.69 gm/cc)	Actual	19.7	18.9	17.3

ATTACHMENT 2

TABLE 2

BORAFLEX QUALITATIVE INSPECTION CRITERIA

Poison insert and lead-in guide assembly:

SFP Location SP-40/41

Total Gamma Dose 1×10^{10} Rads Gamma

Criteria	Comments (Location, Extent, etc.)
1. White milky substance present	Yellow staining on entire length where in contact with stainless sheet, like some sort of dried powder.
2. Missing pieces	No
3. Cracking	Yes - Some observed from cutting and handling; otherwise had good integrity.
4. Powdery substance accumulation in bottom of cladding	No
5. Slumping of boraflex	None
6. Thinning on edges/fraying, strings on edge of boraflex	Not occurring
7. Surface porosity and pitting	None
8. Color: gray vs. black	Some gray patches on edges, which seems to "powder" like the samples did.
9. Friability	Does not crumble, rather it snaps in brittle fashion.
10. Brittleness/flexibility	Brittle, yet will bend over length.

ATTACHMENT 2

TABLE 1

BORAFLEX QUALITATIVE INSPECTION CRITERIA

Poison insert and lead-in guide assembly:

SFP Location SX-47 West
Total Gamma Dose ~0

Criteria	Comments (Location, Extent, etc.)
1. White milkey substance present	White stain entire length, where in contact with the stainless sheet, mostly in middle of ladder fashion.
2. Missing pieces	No
3. Cracking	No
4. Powdery substance accumulation in bottom of cladding	No
5. Slumping of boraflex	No
6. Thinning on edges/fraying, strings on edge of boraflex	No
7. Surface porosity and pitting	No
8. Color: gray vs. black	All black
9. Friability	No
10. Brittleness/flexibility	Very flexible and bends well; breaks when pinched hard over.

ATTACHMENT 2

TABLE 2

BORAFLEX QUANTITATIVE INSPECTION CRITERIA

Poison insert and lead-in guide assembly:

SFP Location SX-47 West
Total Gamma Dose 0

Average Values of		Top	Middle	Bottom
		Location Along Length of Boraflex Sheet		
1. Thickness @ center (inches) (nom. = 0.11")		.093	.094	.099
2. Thickness @ edges (inches)		.091	.104	.096
3. Width (inches) (nom. = 8.0")		7.88	7.88	7.88
4. Weight: IDEAL vs ACTUAL (gms) (Assume $\rho_{boraflex}$ = 1.69 gm/cc)	Ideal	23.9	27.2	21.1
	Actual	22.6	25.7	20.4

POINT BEACH [illegible]EAR PLANT

RADIOLOGI[illegible]URVEYS

LOCATION POISON INSERT SAMPLES

DATE 6-20-86 INSTRUMENT TYPE E-120 A / CAN / SAC-4 PURPOSE: ☐ ROUTINE DAILY SURVEY

TIME 1000 SERIAL NO. 7144 / 783-784 / 7076 ☒ OTHER DETERMINE CAN COUNT ☐ RWP

MONITOR [signature] COUNTED BY [signature]

REVIEWED BY

NO.	MREM/HR	βγ DPM/ 100 CM²	α DPM/ 100 CM²	REMARKS
1	≤2 & 4β	2720		SP-40/41 TOP
2	≤2 & 12β	3285	144	✓ MIDDLE
3	2 & 44β	12,090		BLANK (GRAY AREA)
4	2 & 40β	5835	≤24	SP-40/41 Bottom
5	≤2	440		SX-47 middle
6	≤2	370	≤24	Bottom
7	≤2	160		TOP

SKETCH OF AREA OR ITEM SURVEYED

All Readings in mR/hr.
*Designates Hot Spot

same as above

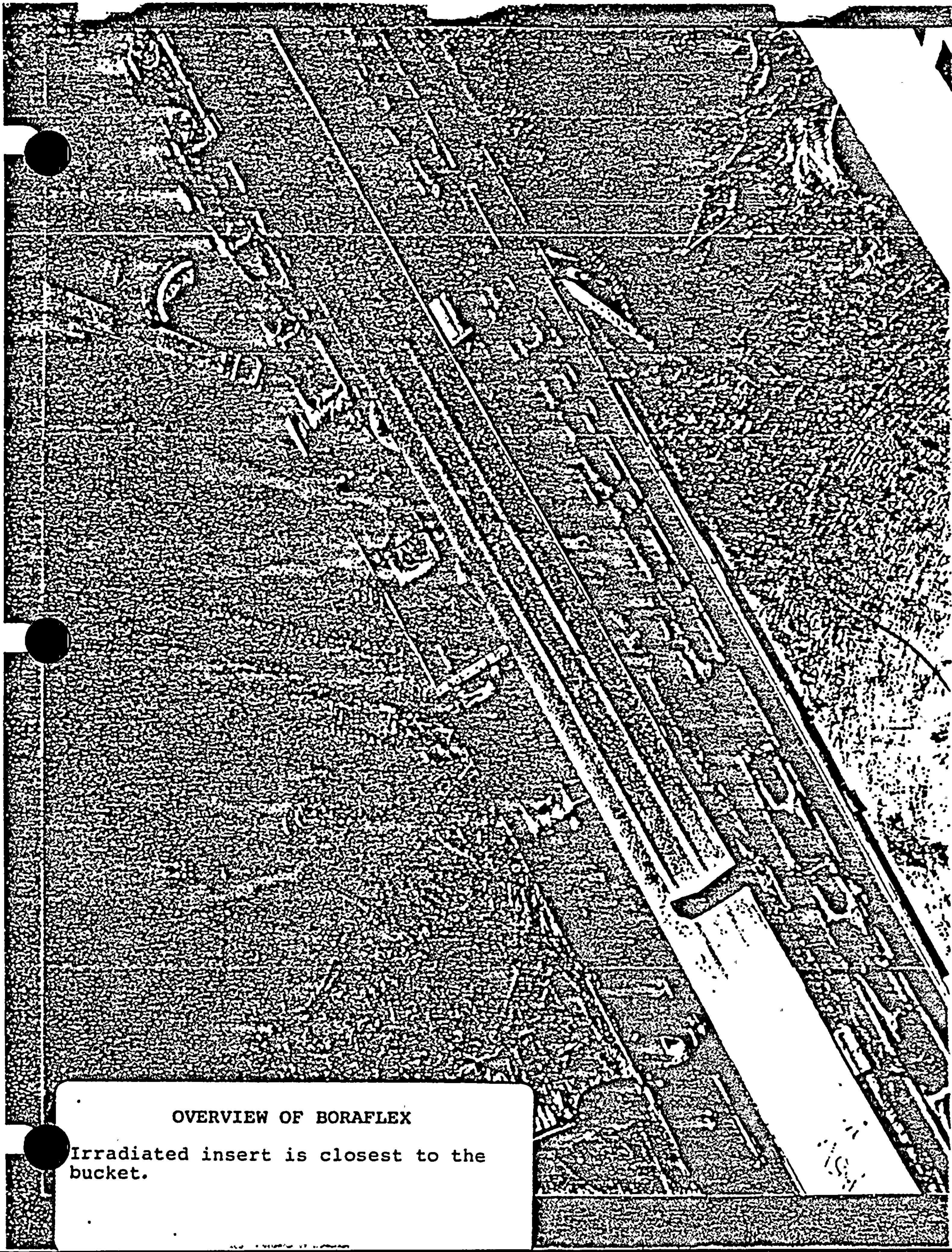
ATTACHMENT 3

ATTACHMENT 4

PHOTOGRAPHS OF FULL-LENGTH BORAFLEX INSERTS

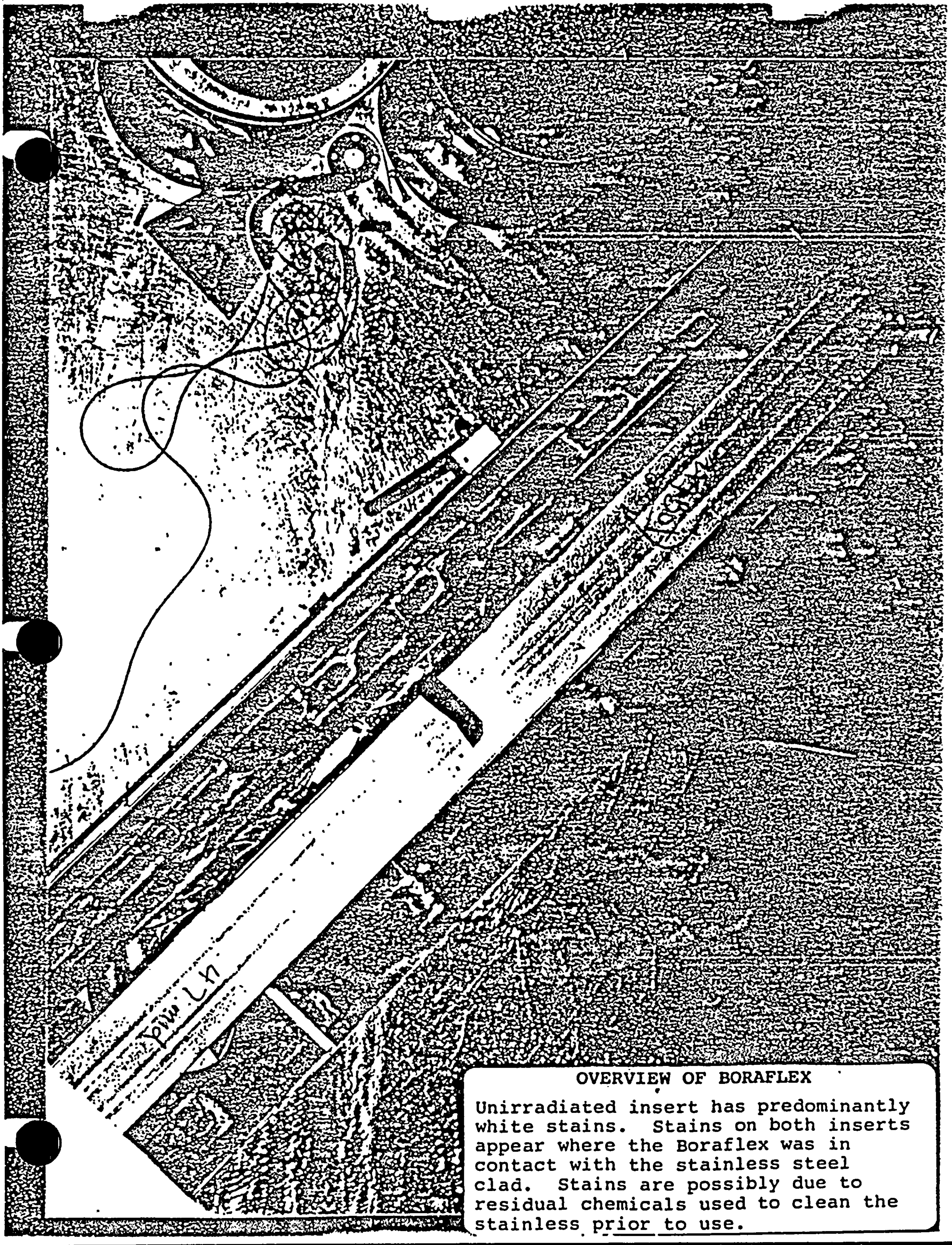
TAKEN DURING EXAMINATION ON

AUGUST 18-20, 1986



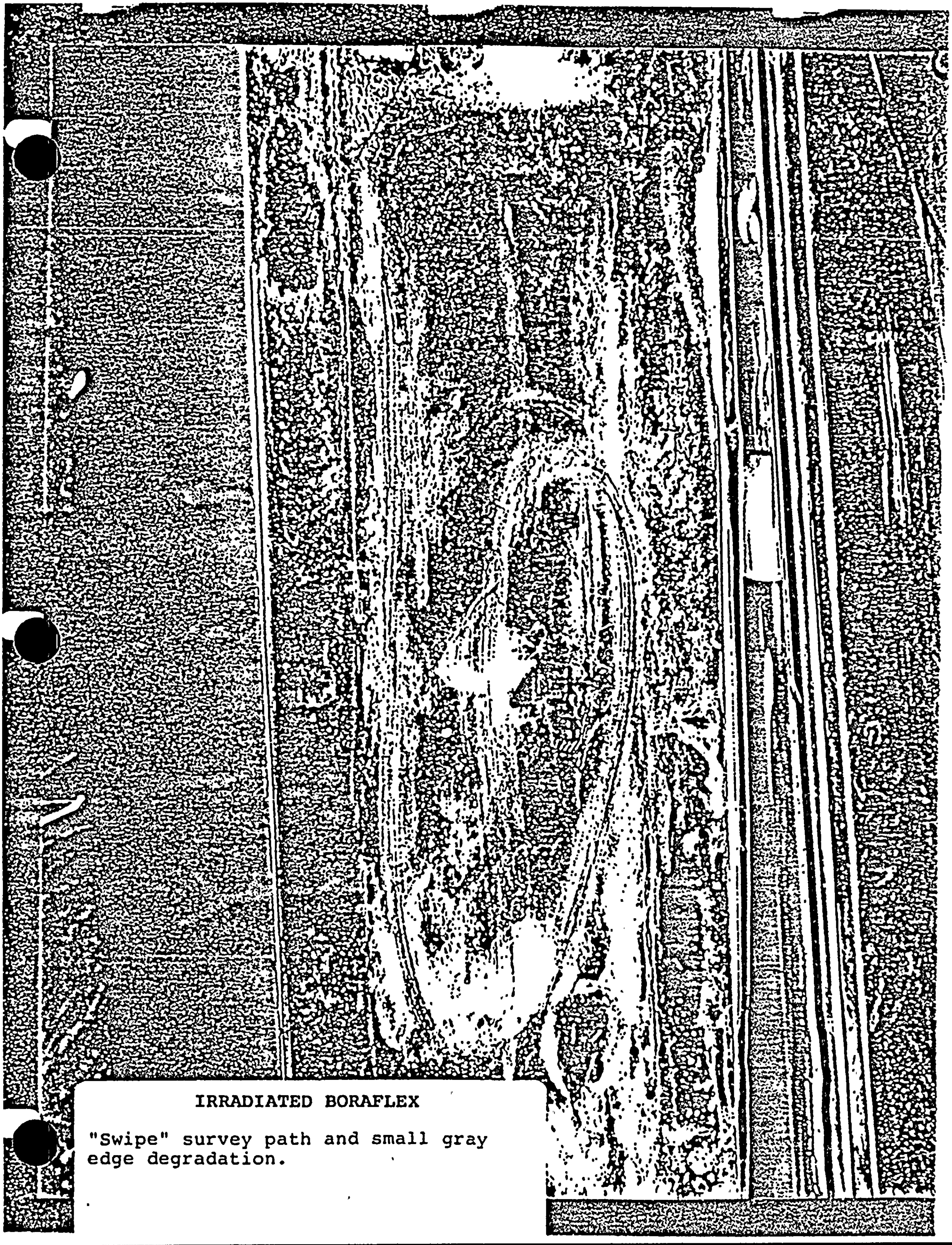
OVERVIEW OF BORAFLEX

Irradiated insert is closest to the bucket.



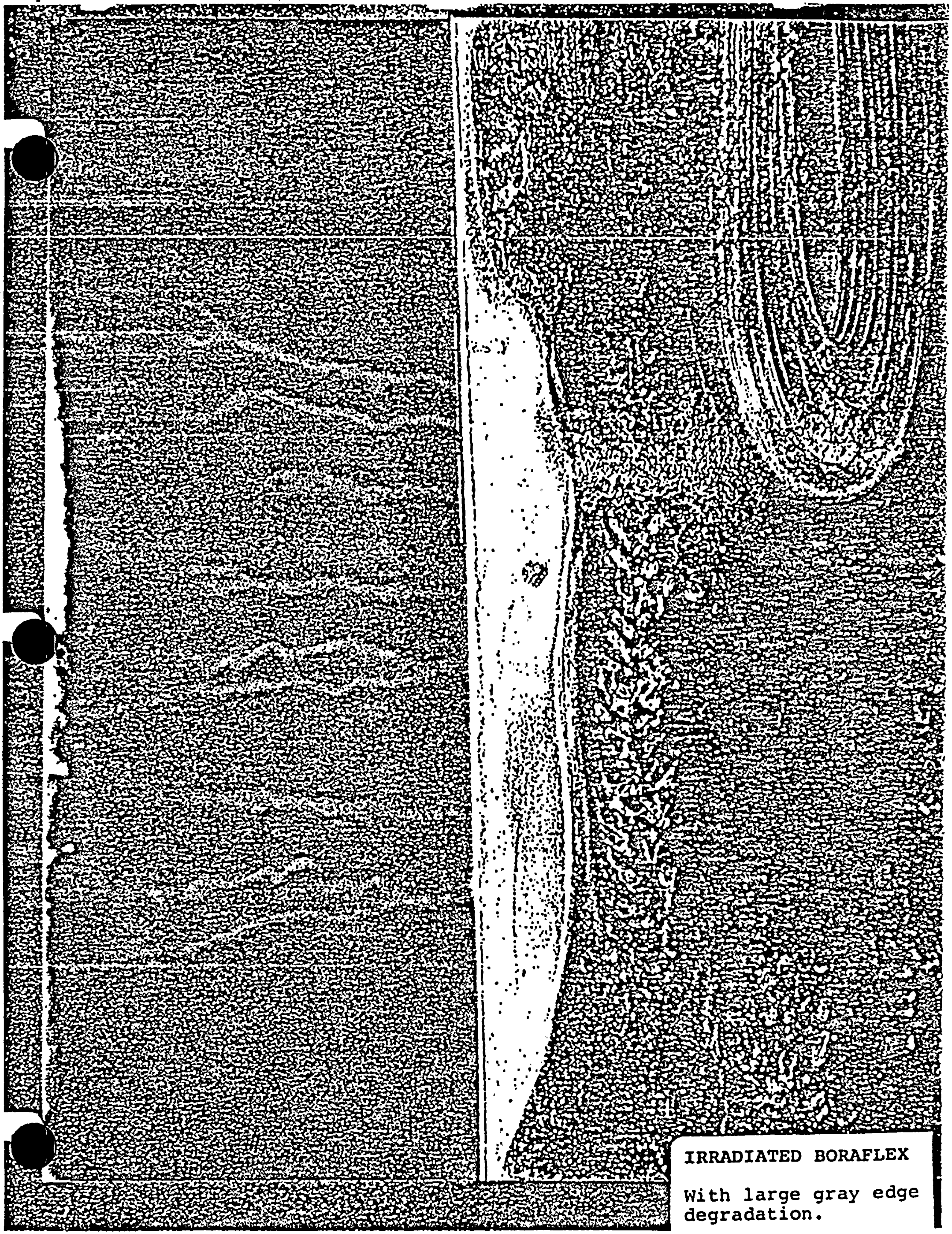
OVERVIEW OF BORAFLEX

Unirradiated insert has predominantly white stains. Stains on both inserts appear where the Boraflex was in contact with the stainless steel clad. Stains are possibly due to residual chemicals used to clean the stainless prior to use.



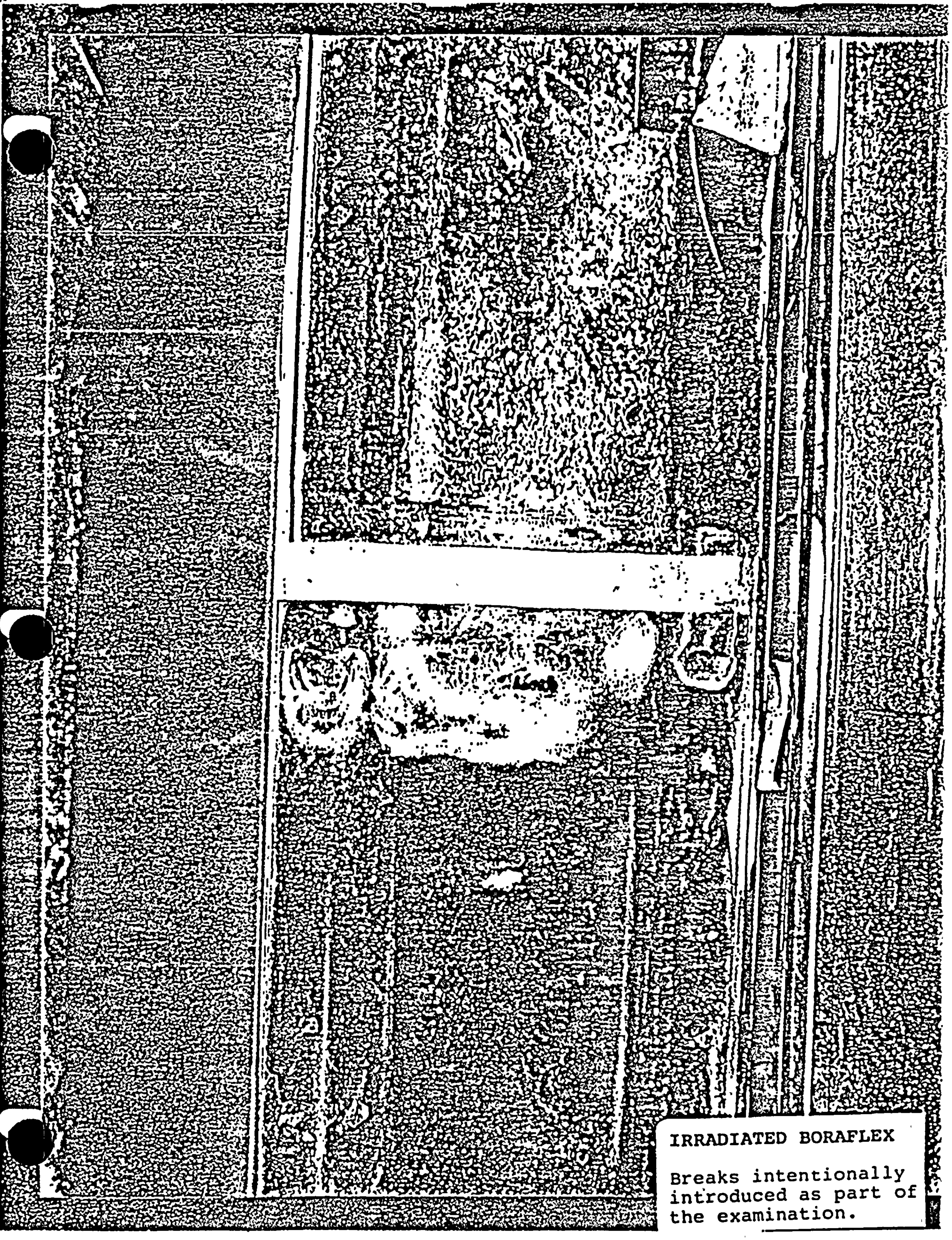
IRRADIATED BORAFLEX

"Swipe" survey path and small gray edge degradation.



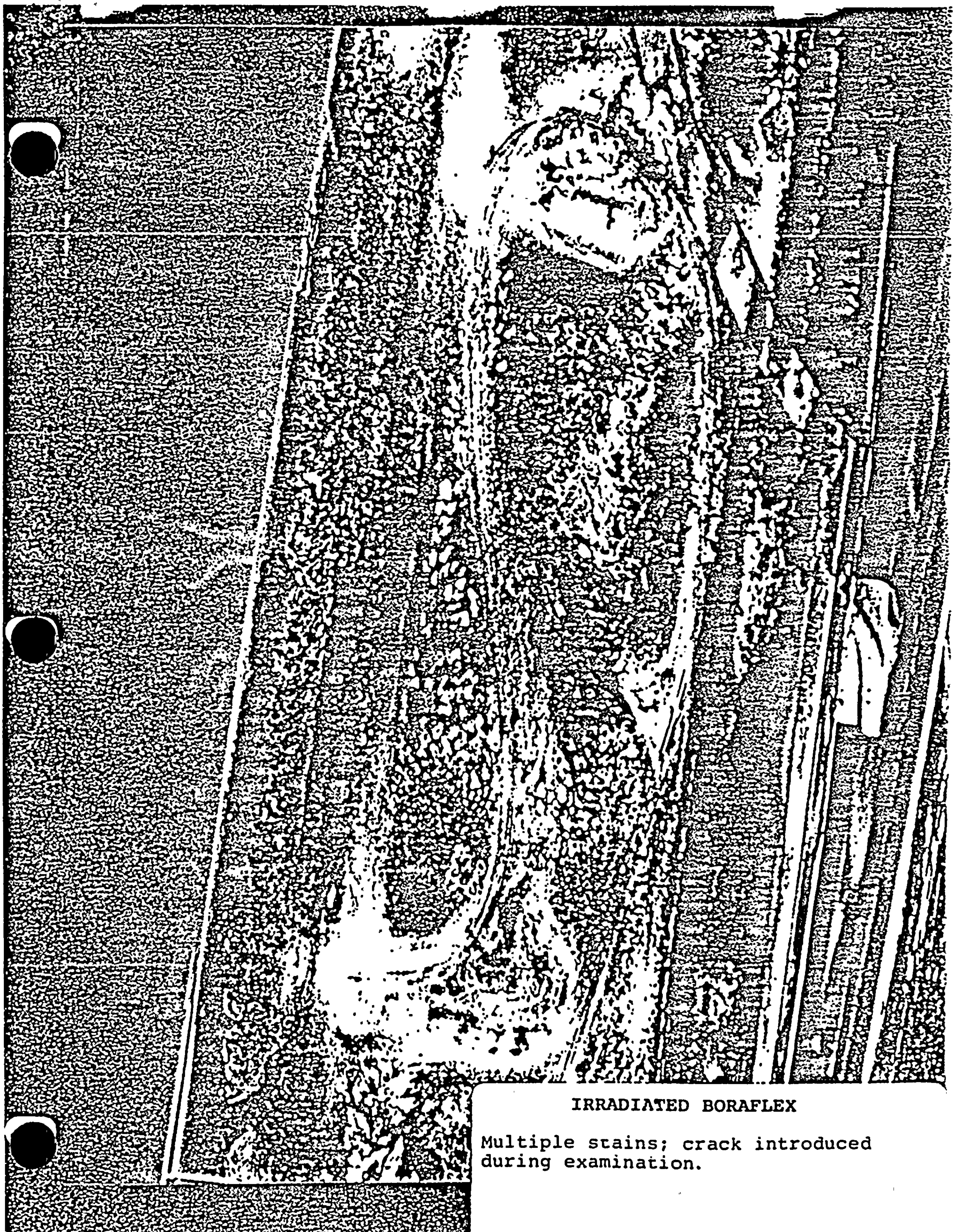
IRRADIATED BORAFLEX

With large gray edge degradation.



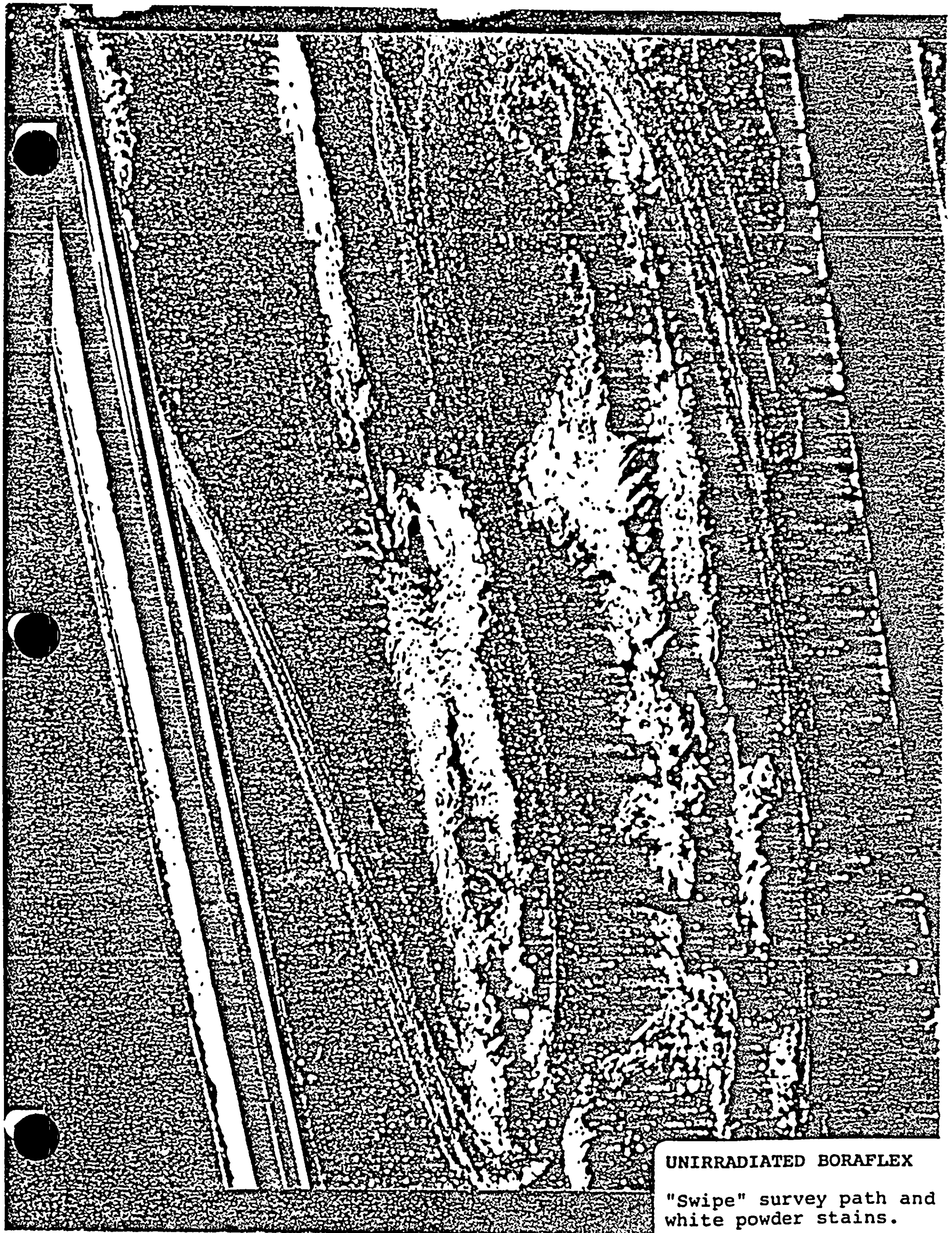
IRRADIATED BORAFLEX

Breaks intentionally introduced as part of the examination.



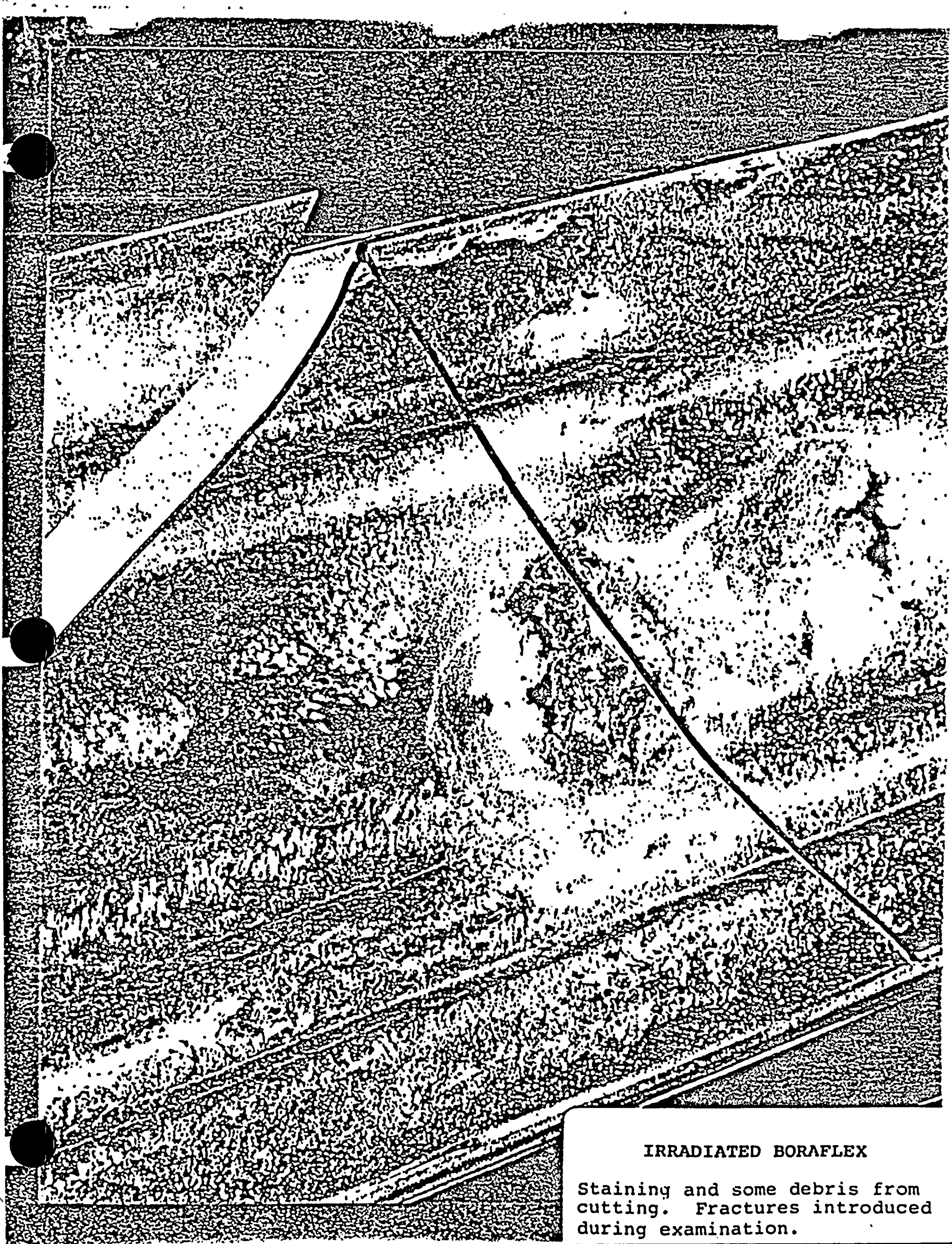
IRRADIATED BORAFLEX

Multiple stains; crack introduced during examination.



UNIRRADIATED BORAFLEX

"Swipe" survey path and white powder stains.



IRRADIATED BORAFLEX

Staining and some debris from cutting. Fractures introduced during examination.