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Water Reactor Divisions
Steam Generator Programs
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LONG-TERM CORROSION TEST PROGRAM

of

NUCLEAR STEAM GENERATOR TUBING SAMPLES

from

THREE MILE ISLAND UNIT 1

to

GPU-NUCLEAR, Reading, PA

FIRST INTERIM REPORT

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1.0 INTRODUCTION

1.1 The Present Program

The GPU Nuclear Corporation (GPU-N) is engaged in a repair program for the nuclear steam generators at its Three Mile Island Unit 1 (TMI-1) generating plant. A part of that program includes the establishment of the long-term corrosion behavior of steam generator tube samples, from the TMI-1 steam generators, under a programmed exposure of representative reactor coolant chemistry and temperature variations. This long term corrosion test (LTCT) program is being conducted for GPU-N by the Westinghouse Electric Corporation through the Westinghouse Steam Generator Programs Activity which sponsors the testing operations at the Westinghouse Corporate R and D Center.

The purpose of this program, as stated in the GPU-N Short Form Specification SP1101-22-008, Revision 2, is to demonstrate that the processes of kinetic expansion and sulfur oxidation during peroxide cleaning and plant operation will not result in propagation of existing IGSCC or initiation of new IGSCC.

The GPU-N Specification SP1101-22-008 was transmitted to Westinghouse under a cover letter of July 13, 1982, by F. S. Giacobbe, Manager, Materials Engineering and Failure Analysis, GPU-N. That cover letter requested that the contractor's program include two interim reports and a final report. The present report is the first of the two interim reports which are structured into the Westinghouse agreements with GPU. This report covers all program activities from inception into May 1983, as delineated in Section 3.0, Program Summary.

1.2 Background Discussion

The 2 nuclear steam generators of the TMI-1 facility are the once-through steam generator (OTSG) design furnished by the Babcock and Wilcox Company. As part of that supplier's manufacturing sequence, the entire finished OTSG is given a stress relief heat treatment, the time and temperature cycle of which creates a grain boundary chromium depleted (GBCD) microstructure in the nickel-chromium-iron alloy (Inconel Alloy 600) which is the tubing material of

the generator. Extensive testing of this microstructure in aqueous environments which can cause elevated temperature caustic stress corrosion cracking (SCC) has demonstrated that the GBCD condition is at least as resistant as, if not more resistant than, the "mill annealed" condition to the typically intergranular caustic SCC form of degradation (References 1-6). Other tests have demonstrated that the GBCD microstructure possesses high resistance to the "Coriou" type of phenomenon, an intergranular cracking process requiring high stress, or high strain, or a high strain gradient, coupled with a typically prolonged exposure at elevated temperatures ($\geq 600^{\circ}\text{F}$) to high-purity water (Reference 7).

The only extensively investigated conditions which demonstrate that the GBCD condition is selectively susceptible to intergranular forms of degradation are at low temperatures (at or near room temperature, for example) in aqueous species which are not representative of normal nuclear steam generator environments. Apart from boiling nitric acid solutions (the "Huey" and "modified Huey" tests), there exist certain sulfur-containing oxyanions which can be deleterious in low temperature aqueous solutions to iron-chromium-nickel alloys in general, if these alloys possess the GBCD structure. In these potentially aggressive oxyanions, the oxidation state of sulfur is less than 6^{+} (or VI), species such as tetrathionate ($\text{S}_4\text{O}_6^{2-}$), thiosulfate ($\text{S}_2\text{O}_3^{2-}$), or "polythionic acid" ($\text{H}_2\text{S}_x\text{O}_y$) having received attention in recent years (References 8 and 9). This form of intergranular attack (which is selective to and requires the GBCD structure) has not been identified for the very common sulfate ion, SO_4^{2-} , however. Definitive observations of the relatively high resistance of the GBCD structure, compared to the "mill annealed" condition, to intergranular attack in acid sulfate solutions have recently been published under EPRI sponsorship. These tests, which used 80,000 ppm Na_2SO_4 at an initial room temperature pH of 3 (obtained with H_2SO_4), showed that the GBCD condition was at least as resistant as the "mill annealed" condition of the same heat, in 5000 hour exposures at 630°F (Reference 10).

The low-temperature reduced sulfur oxyanion attack of GBCD Inconel 600 remains one of the few cases to which the GBCD condition can be demonstrated to be selectively sensitive. A detailed, failure analysis of TMI-1 OTSG tubing

which exhibited primary-side-initiated intergranular attack and intergranular cracking has led GPU-N to conclude that low-temperature sulfur-species attack was responsible (Reference 11). This conclusion is also supported by additional failure analysis reports (References 12, 13, 14, 15). Both References 11 and 12 provide possible sources of an ingress of sulfur species into the reactor coolant system during the prolonged layup of TMI-1, and both documents address mechanistically plausible chemical scenarios for the production of an aggressive aqueous low-temperature sulfur-bearing species. It is the TMI-1 OTSG tubing which has had the history outlined above and detailed in Reference 11 which is the subject of the current LTCT program.

2.0 OBJECTIVES

2.1 Primary Objectives

The two initial objectives of the LTCT program are responsive to the GPU-N Specification SP1101-08-022 and were (1) the determination of the long-term corrosion and stress corrosion performance of service-exposed TMI-1 OTSG tubing material from the generators and (2) the identification of any potential in-plant corrosion issues and the conditions for such issues. The tests are to be performed using reactor coolant chemistry composition representing the upper bound of specified limits for contaminants. GPU-N Specification SP-1101-08-022 provides the chemistry limits and time and temperature cycles for the tests.

To meet program objectives four types of specimens were utilized in four separate test vessels. Specimens consisted of full section, axially loaded "Lead Test" and "Repair Test" specimens, C-ring, and U-bend specimens. "Lead Test" and "Repair Test" specimens were prepared from service exposed Unit 1 steam generator tubing which had been removed from the upper tubesheet region. "Lead Test" specimens consisted of open lengths of tubing while "Repair Tests" specimens consisted of tube/tubesheet mockups prepared by explosively expanding tube sections into an outer collar following a procedure which duplicates repairs performed on Unit 1. C-rings, which were loaded to place I.D. surfaces in tension, were prepared from both service exposed and archive (non-service exposed) tubing. U-bends were prepared from other materials used in the fabrication of Unit 1 core structural components. The test operational sequence and chemical compositions of the solutions used for each test simulated conditions encountered in plant operations and were, with minor variations, identical in all tests. The only difference between test environments was that one contained thiosulfate and the remaining three contained sulfate additions.

2.2 Additional Objectives

Additional secondary objectives, not originally included in GPU-N SP1101-08-022 have been identified and met as the LTCT program and on-site

operations at TMI-1 have proceeded. The chief of these secondary objectives became the development of equipment for and the achievement of the hydrogen peroxide cleanup of selected OTSG samples for the subsequent inclusion of such cleaned samples into the LTCT.

Another secondary objective which is an outgrowth of the preceding cleanup activity became and is the verification of the performance of stressed alloys representative of in-core materials when such materials are (1) pre-exposed to a "conditioning" of reactor coolant (containing approximately 100 ppb of SO_4), (2) exposed to the hydrogen peroxide cleanup cycle, and (3) subsequently exposed for prolonged periods to the "worst case", but normal, reactor coolant chemistry programmed by (and identical to) the main LTCT program.

A third secondary objective was to determine, using Auger electron spectroscopy (AES), how much sulfur (in $\mu g/cm^2$) is present within the first 100 nm of the inside (ID) surfaces of GPU-N steam generator tubes that were conditioned to simulated reactor coolant chemistry at elevated temperatures, using standards prepared by ion implantation to calibrate the AES technique, and X-ray photoelectron spectroscopy (XPS) to identify the sulfur compound(s) present.

3.0 PROGRAM SUMMARY/PLAN

The program plan has undergone several iterations, modifications and alterations of scope since its inception under the original GPU-N Specification SP1101-22-008. As presently structured, the program consists of three principal elements.

1. Two extended duration "Lead Tests" using "Lead Test Samples", as defined in GPU-N SP1101-22-008. These tests started in October, 1982, and are continuing.
2. A hydrogen peroxide cleanup run to simulate the treatment of the TMI-1 primary system. This test applied to two "Repair Test Samples" and one "Lead Test Sample", as defined in GPU-N SP1101-22-008, and "Core Material Samples", as described in this report. It was completed in March 1983.
3. Two additional "Lead Test Type" extended-duration corrosion tests using the "Repair, Lead, and Core Material Samples" of Item 2, preceding. These tests started in May 1983 and are continuing using the same "Lead Test" operational sequence as the Item 1 tests.

The present report encompasses Item 1 through May, 1983, and the entirety of Item 2. Item 1 remains in progress and Item 3, as noted, is underway.

Item 1, the two long-term "Lead Tests", follows essentially the plan originally given in GPU-N SP1101-22-008 and has consisted of two tests which differ only in the make-up sulfur-dosing species to the otherwise normal reactor coolant simulated chemistry (Li, B, H₂, etc.). Test 1 uses thiosulfate and Test 2 uses sulfate. Both sulfur anions are at trace levels (100 ppb, nominally). Both tests follow the same operational sequences which are:

- (1) Hot Functional Test (HFT) Stage
- (2) Cycle 1
- (3) Cycle 2
- (4) Cycle 3
- (5) Cycles 4-6.

(The cycles differ in the amount of B, as H_3BO_3 , and Li, as LiOH, which are present in the test solutions and which are varied to simulate plant operations.)

This report covers the 2 lead tests, Item 1, from inception through the HFT and further through Cycles 1 and 2. As noted, the report also covers the hydrogen peroxide cleanup testing, Item 2, and, as such, thereby delineates the test matrix (of samples) which constitutes Item 3, the in-progress lead test type program with the peroxide-cleaned samples.

4.C FACILITIES DESCRIPTION

4.1 Once-through System

The once-through system shown schematically in Figure 4-1 and in the photograph of Figure 4-2 is the basic apparatus used for all long term corrosion testing of GPU-N OTSG Inconel tubing. The basic element of this apparatus is a standard Autoclave Engineers 2-liter, bolted closure autoclave, which contains the test specimens. These specimens, which are samples of axially loaded GPU-N OTSG Inconel 600 tubing, and cans of C-ring or U-bend samples (depending on the individual test specifications), are plumbed for a series flow of solution upward through the samples. Entry ports (feed-throughs) in the autoclave head provide the means of nitrogen gas pressurization of the bellows of the specimen loading fixture as well as entry and egress of the tubing which carries the test solution to and from the specimens.

The first item in succession of the flow-through apparatus is a stainless steel makeup tank (MUT) with a nominal 70 l capacity, which is filled with 50 l of the test solution. The MUT is equipped with a sight tube to monitor the liquid level of the test solutions, and ports to provide means of solution exit, sparging, and pressurizing (gas overpressure). The second item in series, following the MUT is a Whitey Model LP10 feed pump which is adjusted to maintain a 100 ml/h (ideal) flow of the test solution through the system. The test solution flows through a check valve, into the autoclave, internally through the specimens, and exits the autoclave through a cooler composed of coiled stainless steel tubing. The cooler effluent discharges through a Controlmatic back pressure (BP) regulator, which provides the method of regulating the solution pressure. Located down-stream from the BP regulator is a tap for effluent sampling and, piped in parallel, a flow meter (F/M) to measure system flow rate. Finally, the effluent is collected, monitored and disposed of in accordance to Nuclear Regulatory Commission requirements.

Ports on the autoclave body are used for filling, evacuation, sparging and for the attachment of the rupture disk (R/D) and BP regulator necessary for controlling the autoclave pressure. Both the autoclave rupture disk and the

BP regulator are plumbed to the radiation monitored collection drum for safety in event of an overpressure release.

The autoclave is heated by means of external clamp on resistance heaters. Normal safety and control equipment are used with each autoclave system.

This basic system has been used to conduct both the HFT and Lead Test Operations Cycles 1 and 2 (CFDA-82-353 and CFDA-82-370 respectively) for Lead Tests 1 and 2. The detailed operating procedures for HFT and operations cycles are presented in Appendix 10.1 and 10.2, respectively.

4.2 Recirculating Peroxide Loop

It is planned to expose the primary system of TMI-1 to a hydrogen peroxide solution to ensure that any residual sulfur species will be oxidized to the sulfate form prior to system heat up. GPU-N elected to have the test specimens for Tests 3 and 4 of the existing program also exposed to this peroxide clean up operation.

In order to accomplish this, the once-through systems of Tests 3 and 4 were modified to produce a series recirculating system. Additional changes to the loop system during the peroxide cleaning cycle were made to improve operating efficiency or to meet contingencies. The peroxide (H_2O_2) loop cleaning system, in its final form, is delineated in Figure 4-3, and shown photographically in Figure 4-4.

In essence, the H_2O_2 loop consisted of two once-through systems in a series loop fed by a single make-up tank. As previously described for the once-through system, the flow of the H_2O_2 cleaning solution through the GPU test specimens within the autoclaves was in a series configuration.

The circuit flow from the MUT, through the autoclave and back to the MUT is straight-forward. The test solution is pumped from the MUT by a circulation pump at the rate of ~7 l/h. A rupture disk, plumbed to return the test solution to the MUT in the event of over pressurization of the system is located downstream from the pump. It is followed by a stainless steel surge

bottle half filled with inert gas, the function of which is to dampen pressure fluctuations resulting from pump operations. The test solution, which is pre-heated by flowing through a regenerative heat exchanger and heating tape covered tubing prior to entering the first autoclave, flows serially through the GPU-N specimens and exits the autoclave. The solution flow through the second autoclave and GPU-N specimens is similar to that of the first autoclave. After leaving the second autoclave, the hot test solution again enters the regenerative heat exchanger, with the purpose of heating the solution about to enter the first autoclave. Following the regenerative heat exchanger in the loop in the order stated are a cooler, a BP regulator to control the test solution pressure, a flow meter, a 4-way valve, a chemical addition system, and the MUT. The normal solution flow direction is upward through the stainless steel chemical addition pressure vessel to assure complete addition of the chemicals.

It is appropriate to note the valving arrangements at the autoclaves which permitted preconditioning of the loop tubing with the autoclaves and samples isolated. Also note-worthy is the tubing from Autoclave 4 to the MUT return line, necessitated by the leakage of a Repair Test sample tube weld. This circuit returned to the MUT the very small volume of solution passing through the weld defect and, thereby, maintained the ΔP across the tube constant.

One of the first revisions to the apparatus was the addition of an automatic chemical injector which allowed continuous addition of hydrogen peroxide (H_2O_2) to the loop and eliminated the need for discrete hourly manual H_2O_2 additions. It was also necessary to add a recirculation pump to assure rapid mixing of all chemical additions to the system.

Other valving and port arrangements in the chemical addition and loop system permitted pressurization, evacuation, and chemical pressure vessel drainage when necessary.

The final system was a product of continuous refinement and improvement throughout the 500 hour peroxide cleaning (exposure) operation.

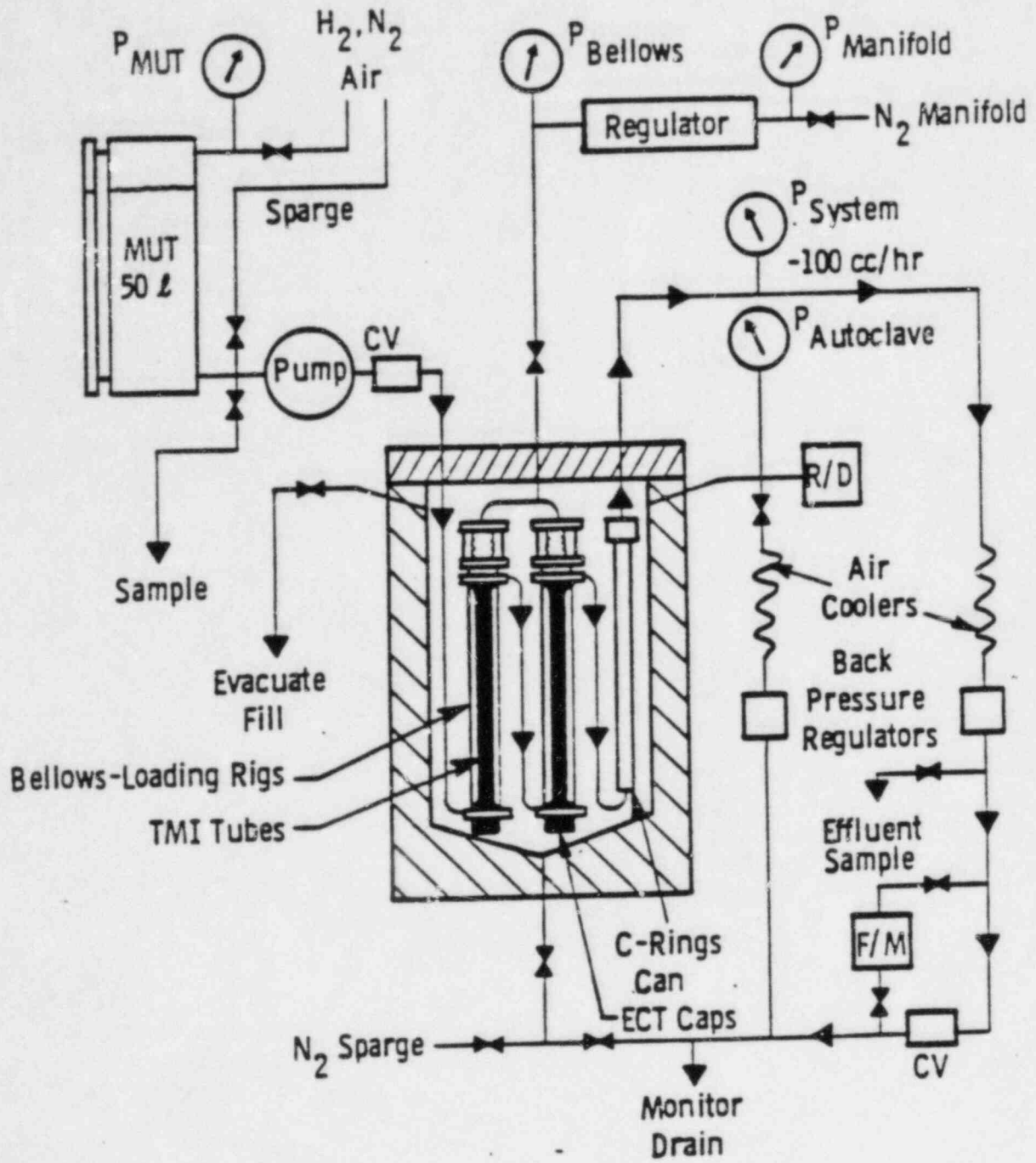


Figure 4-1

Autoclave and Refreshed Sample Stringer with Axial Loading

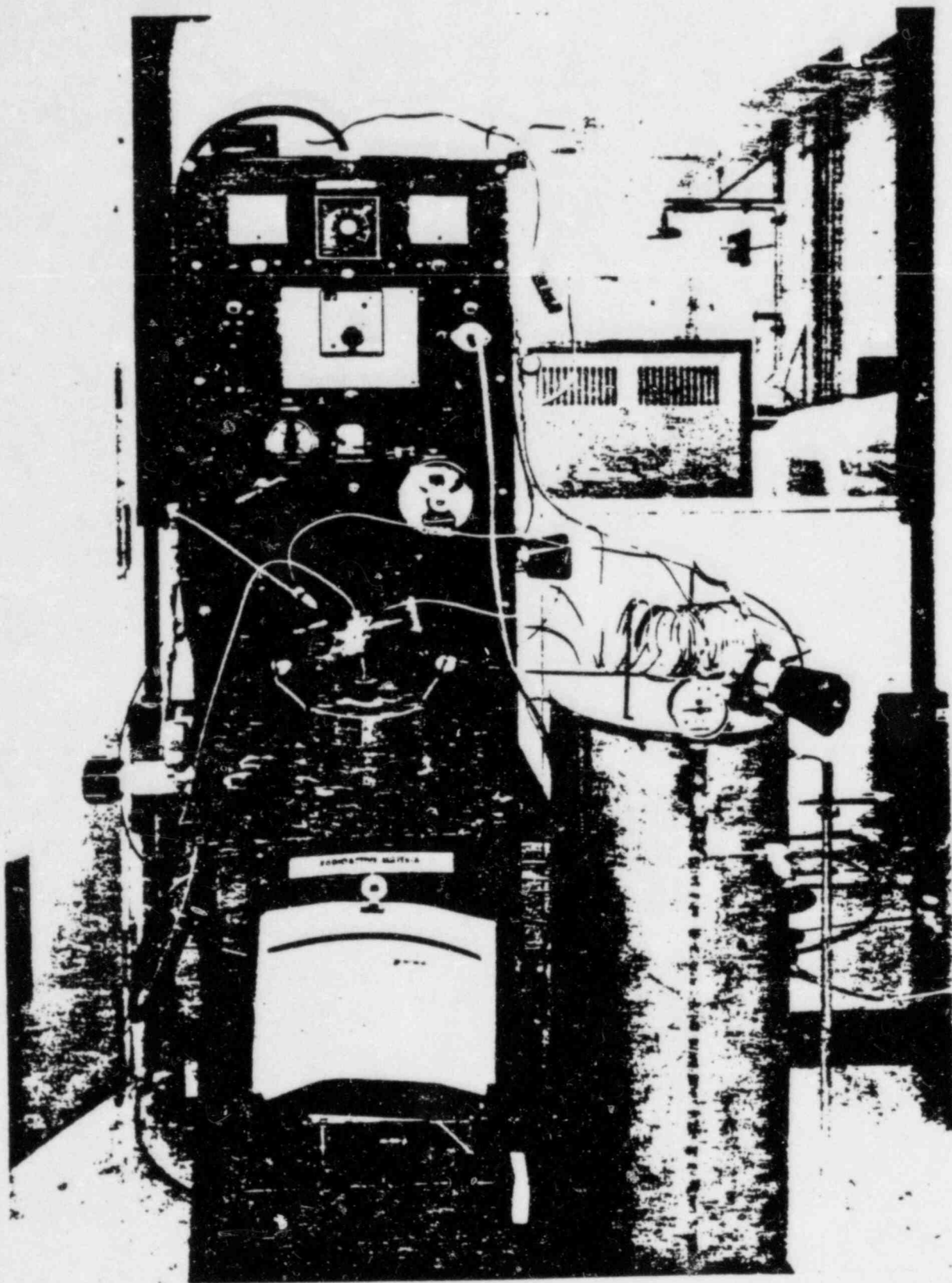


Figure 4.2. Refreshed Autoclave System Used for Once-Through Solution Flow Through the Sample Stringer

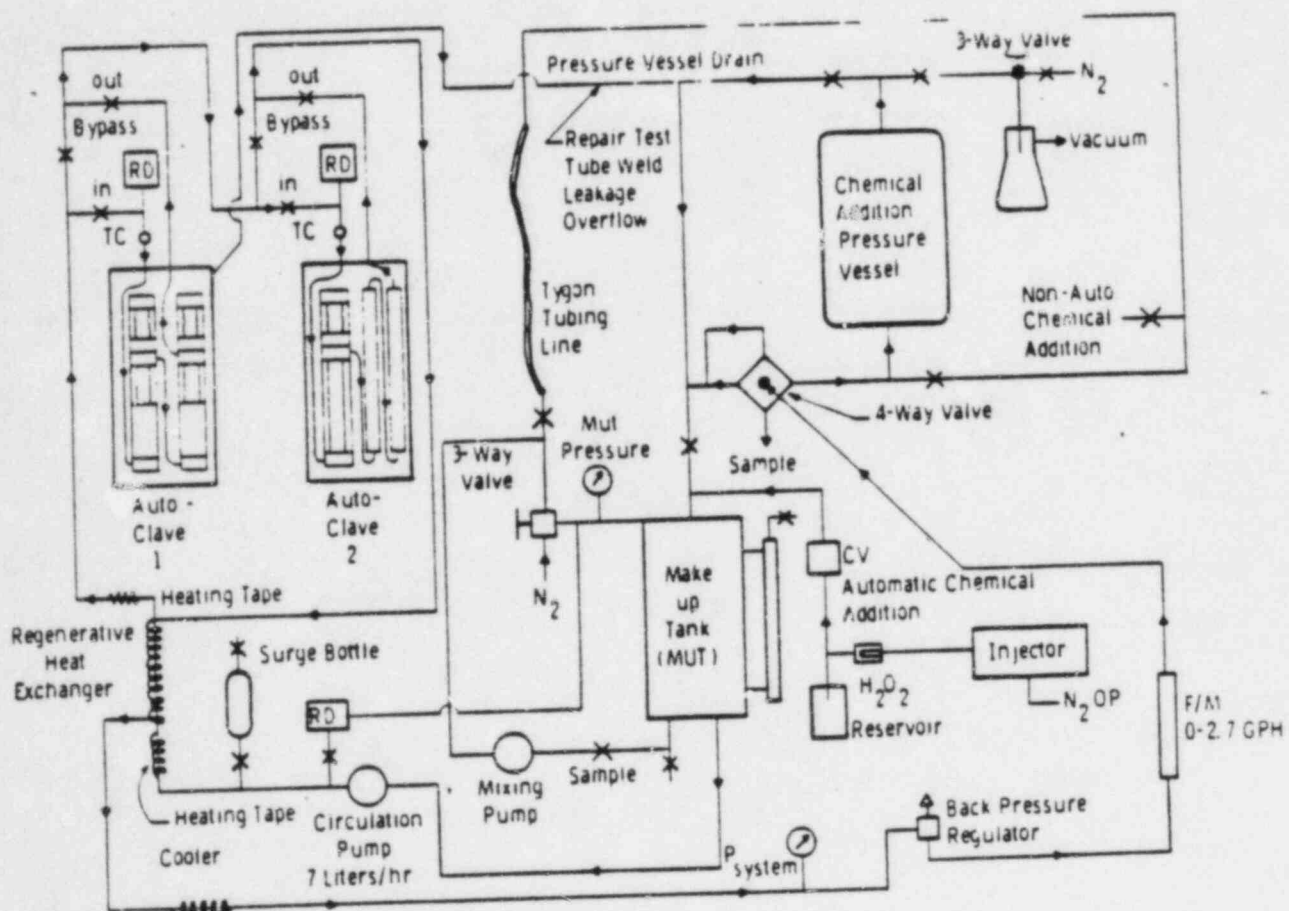


Figure 4-3
 H_2O_2 Loop for GPU-N OTSG Tube Corrosion Tests

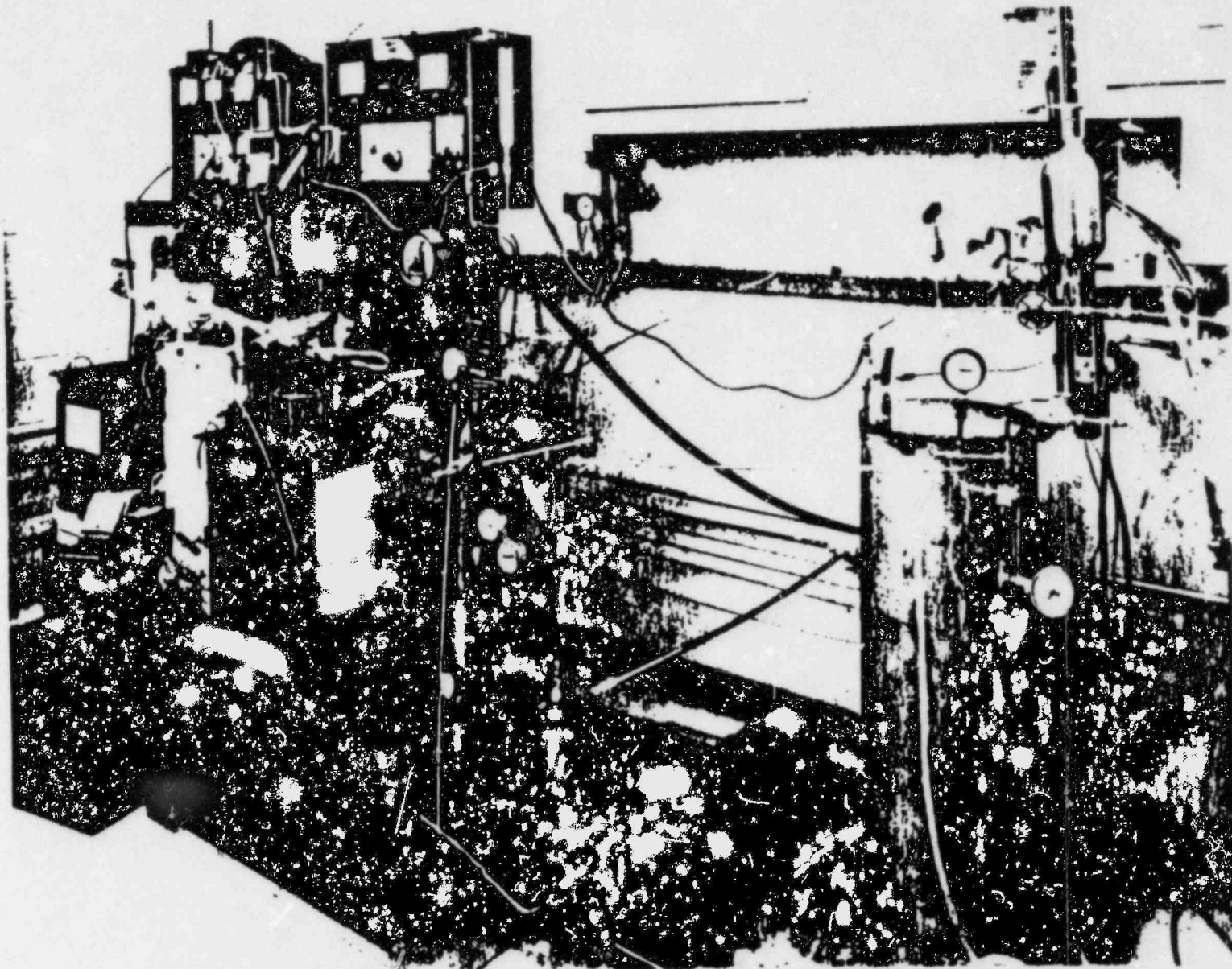


Figure 4.4. Hydrogen Peroxide Loop System Consisting of Two Autoclaves Containing Specimens Assembled for Series Flow

5.0 SPECIMENS AND ENVIRONMENTS

5.1 Materials

Test materials included Inconel 600 steam generator tubing and various reactor core materials. The steam generator tubing was supplied by GPU-N either as sections removed from TMI-1 or as archive OTSG tubing. Tubes from TMI-1 were supplied both with and without eddy current detected defects. The defects were ID-initiated, circumferential cracks, some of which were through-wall. Tubes for full size specimen testing were received with end pieces welded on. The archive tubing previously had been mill annealed plus stress relieved at 1150°F for 18 hrs.

Photographs of the as-received tubes are shown in Figure 5-1. The identifications of the full size tubes are given in Table 5-1. Table 5-2 presents the identification of material used to make C-rings.

The compositions of the reactor core materials used to prepare mini-U-bends are given in Table 5-3. The only material that could not be traced to a heat number and composition was wire which was labeled 308L. An analysis made on the scanning electron microscope with the energy dispersive X-ray spectrometer (EDS) was consistent with the wire being 308L. In Table 5-4 are given the alloy supplier, heat number or heat treatment code, and alloy form. The heat treatments used and the mechanical properties are tabulated in Table 5-5 and the coding of the specimens in Table 5-6. All heat treatments by Westinghouse were in dry hydrogen.

5.2 Sample Configurations

Specimens were configured as stressed, full size tubes, C-rings and U-bends. The full size tubes were supplied by GPU-N in either a "lead" or "repair" test configuration.

5.2.1 Full Size Tubes In the present LTCT, the "Lead" specimens correspond to the free standing tubes in the steam generator while the repair tests

simulate explosively expanded tubing within and just below the tubesheet. All of the specimens were lead type except 894-27 (1/2 to 6-1/2).

Both types of specimens were tested under a 500 pound load except during temperature cooldowns to ambient when the load was increased to 1100 lbs. These loads are representative of those which would exist on OTSG tubes during operation and normal cooldowns, respectively. Loads were obtained with a bellows actuated rig which allowed remote adjustment at any time.

Photographs of the bellows assemblies for each specimen type are shown in Figures 5-2 and 5-3. By pressurizing the bellows, an axial tensile load can be placed on the tube. Each bellows assembly was calibrated prior to use by pressurizing to 3000 psi and measuring the resulting specimen deflection. Specimen load was then be calculated from the elastic modulus and dimensions of the tube.

5.2.2 C-Rings Inconel C-rings were made from 3/4" lengths of tubing per the schedule shown in Table 5-2.

After transversely cutting, each specimen was drilled to take a loading stud and then slotted. The loading method is illustrated in Figure 5-4. An Inconel 600 stud protruded from a hole in the tube at 90° to the desired stress location. The stud was held in place with a nut inside the tube and a locating depression diametrically opposite the stud hole. The C-ring was loaded by turning the stud while holding the nut stationary.

After loading the C-ring, a second Inconel 600 nut was used to lock the stud into place.

Three archive and four service tube C-ring specimens were strain gaged to determine the relationship between specimen strain and opening displacement.

Initially, a biaxial gage was applied to an archive specimen with the following results:

<u>Deflection (mils)</u>	<u>$\epsilon_{\text{circumferential}}$ (μ strain)</u>	<u>ϵ_{axial} (μ strain)</u>
0	0	0
-	286	8
3.3	573	10
-	1146	8
10.0	1718	4
-	2291	6
16.6	2864	4

This test indicated that the axial strain component was insignificant. Only uniaxial gages in the circumferential direction were applied to the remaining specimens.

An LVDT-based diameter measuring device was developed and calibrated for determining specimen displacement. Using this device the strain vs. displacement curves shown in Figure 5-5 were determined. Displacement was limited to 7 mils to avoid gross plastic deformation of the specimens. Subsequent tests verified that the strain vs. displacement relationship remained linear to at least twice this displacement value.

Based on the minimal scatter shown in the strain gage data, all specimens were loaded to a displacement of 13.7 mils prior to autoclave exposure. This value was extrapolated from Figure 5-5 to meet the request of GPU-N to strain the C-rings to 0.25 percent (2500 μ strain).

All C-rings were weighed to the nearest 10 μ g and macrophotographs of the stressed ID area were taken.

The test configuration for the OD loaded Zircaloy 4 C-ring is shown in Figure 5-6. The specimen deflection used was 0.08 inches which is about 25 percent above the yield strain of the material. Type 304 stainless steel bolts and nuts were used to load the Zircaloy 4 C-rings.

5.2.3 U-Bend Specimens Various reactor core materials were included in the experiment as miniature U-bend specimens.

The blanks for mini-U-bends were approximately 1.5" x 0.25" x 0.030". For specimens with welds, the filler metal was deposited by the TIG process at a location corresponding to the eventual apex and element of the U-bend. A U-bend was made by bending the blank around a 1/8-in. diameter mandrel and bolting the legs parallel with an austenitic stainless steel nut and bolt.

Figure 5-7 is a photograph of all of the U-bend specimens.

5.3 Test Solutions

5.3.1 Lead Test Solutions The preparation of the Lead Test solutions followed a systemized procedure which is briefly summarized here. A comprehensive description of the Lead Test Solution preparation is given in the Appendix 10-3.

Stock solutions were prepared from the reagent grade salts of lithium hydroxide monohydrate ($\text{LiOH}\cdot\text{H}_2\text{O}$), sodium fluoride (NaF), sodium chloride (NaCl) sodium thiosulfate pentahydrate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) and sodium sulfate decahydrate ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$).

The nominal concentrations of the stock solutions were 5000 ppm Li^+ , 1000 ppm F^- , 1000 ppm Cl^- , 1000 ppm $\text{S}_2\text{O}_3^{2-}$, and 1000 ppm SO_4^{2-} .

In preparing an individual Lead Test solution, a weighed amount of United States Borax and Chemical Company Special Quality boric acid was dissolved in deionized water in a polyethylene holding tank. Aliquot volumes of the Li, and SO_4 (or S_2O_3 , depending on the test solution) stock solutions were added and the solution in the holding tank was deaerated by sparging with nitrogen. Prior to transfer of the test solution from the holding tank to the MUT, and just prior to the test startup, a weighed amount of 65 percent aqueous solution of hydrazine (N_2H_4) and an aliquot volumes of F^- and Cl^- were added to an in-line addition vessel. During the transfer process, these species are mixed with solution from the holding tank and flushed into the MUT. This procedure was used to minimize the loss of hydrazine and to avoid adsorption of F^- and Cl^- on the walls of the polyethylene holding tank.

The nominal chemical compositions for the individual Lead Test solutions are given in Table 5-7. The sulfur species for "Solution 1" (GPU-N designation) is exclusively thiosulfate as shown in Table 5-7; for "Solution 2" it is exclusively sulfate.

5.3.2 Hydrogen Peroxide (H_2O_2) Solutions The 500 hour pre-operational exposure of the GPU-N specimens to hydrogen peroxide solution was performed in a recirculating loop system according to the detailed operating procedure delineated in Appendix 10-4.

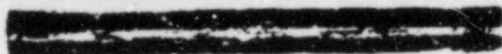
The initial composition of the 50 l of solution in the MUT consisted of 2350 ± 50 ppm boron (as H_3BO_3), 1.8 to 2.2 ppm lithium (as LiOH) and 0.100 ± 0.05 ppm sulfate (as Na_2SO_4). The lithium and sulfate (SO_4) were added as aliquots of the stock solutions described in Section 5.3.1. The pH of this solution was adjusted to 8.0 - 8.2 with concentrated (28 - 30 percent NH_3) ammonium hydroxide (NH_4OH).

Hydrogen peroxide (H_2O_2) initially was added manually to the loop in hourly increments. Subsequently an automatic, chemical addition system was used to make periodic additions of a 50,000 ppm H_2O_2 stock solution. The peroxide stock solution was prepared by weighing 166.7 g of Perone*30 EG hydrogen peroxide (30 percent H_2O_2 by weight) into a 1 liter volumetric flask and diluting to volume with water. All of the water used for solution preparation and dilution was high purity deaerated deionized water, with a conductivity of ~ 0.1 mho.

Other procedures required for test operation during the peroxide exposure are also found in Appendix 10-4.

* E. I. DuPont de Nemours, Inc., Industrial Chemical Division, Wilmington, Del.

29-27 18'-24 1/2"



A-14-69 2'-6 1/2"



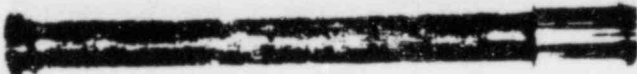
B-11-62 237 5/8-240 5/8



A-13-63 38 5/8-42 1/8 0°



A-88-7 Pc 2-9 3/4



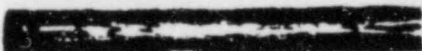
A-88-7 Pc 9 3/4-12 1/2



A-2-6-9 Pc 10'-10 5/8



A-2-6-9 Pc 25'-30 1/2



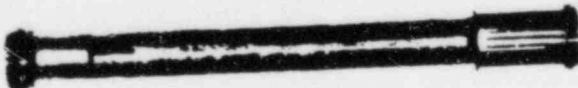
A-13-63 Pc 11'-20 1/2



A-13-63 Pc 20 1/2-23 1/2



B-6-22 Pc 52'-59' 0°



B-16-22 Pc 59'-64'

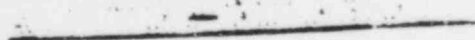
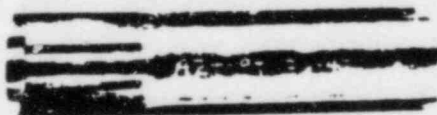
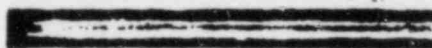
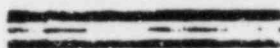
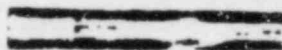
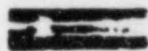
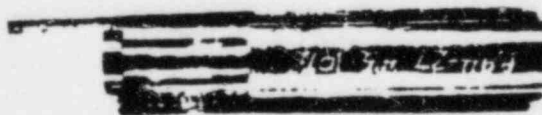


Figure 5.1. Photographs of As-Received Material



A24-94 36-42



B94-27 4-1/2-10-1/2

Figure 5.1. Photographs of As-Received Material (Continued)

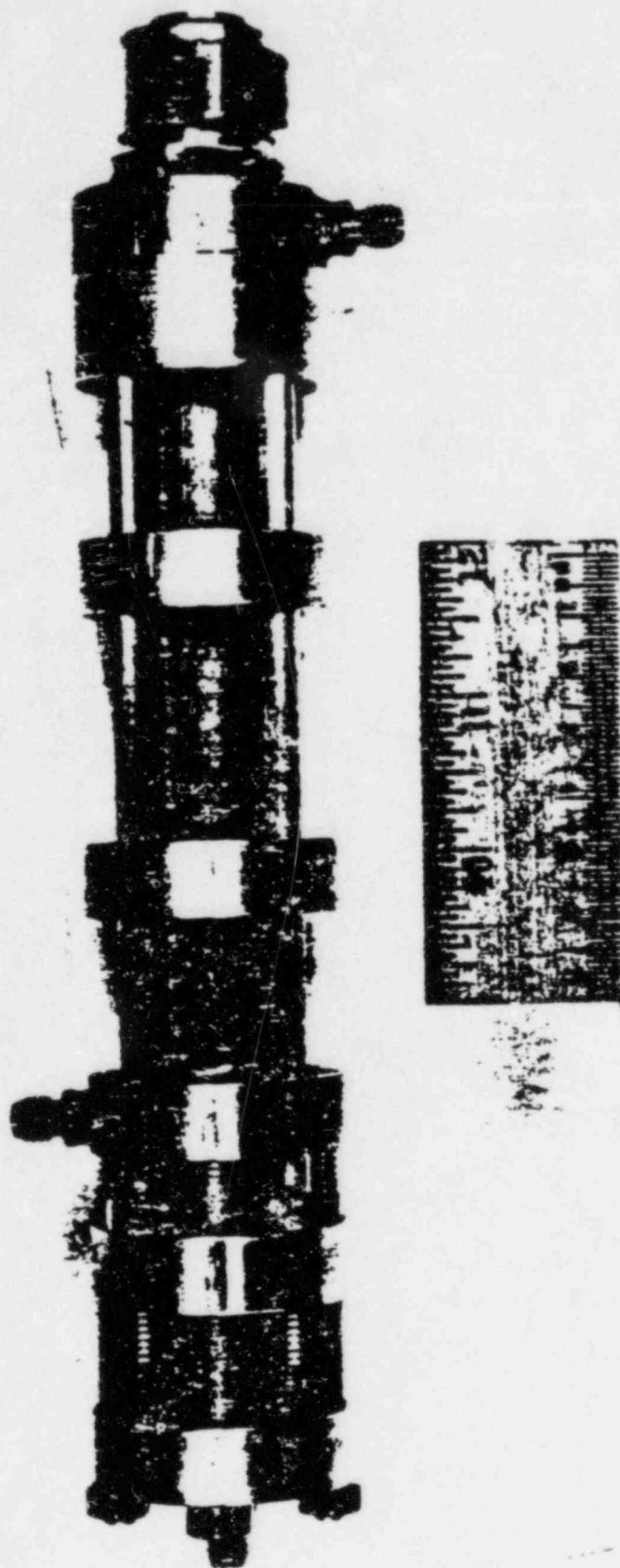


Figure 5.2. Lead Test Specimen Bellows Loading Assembly

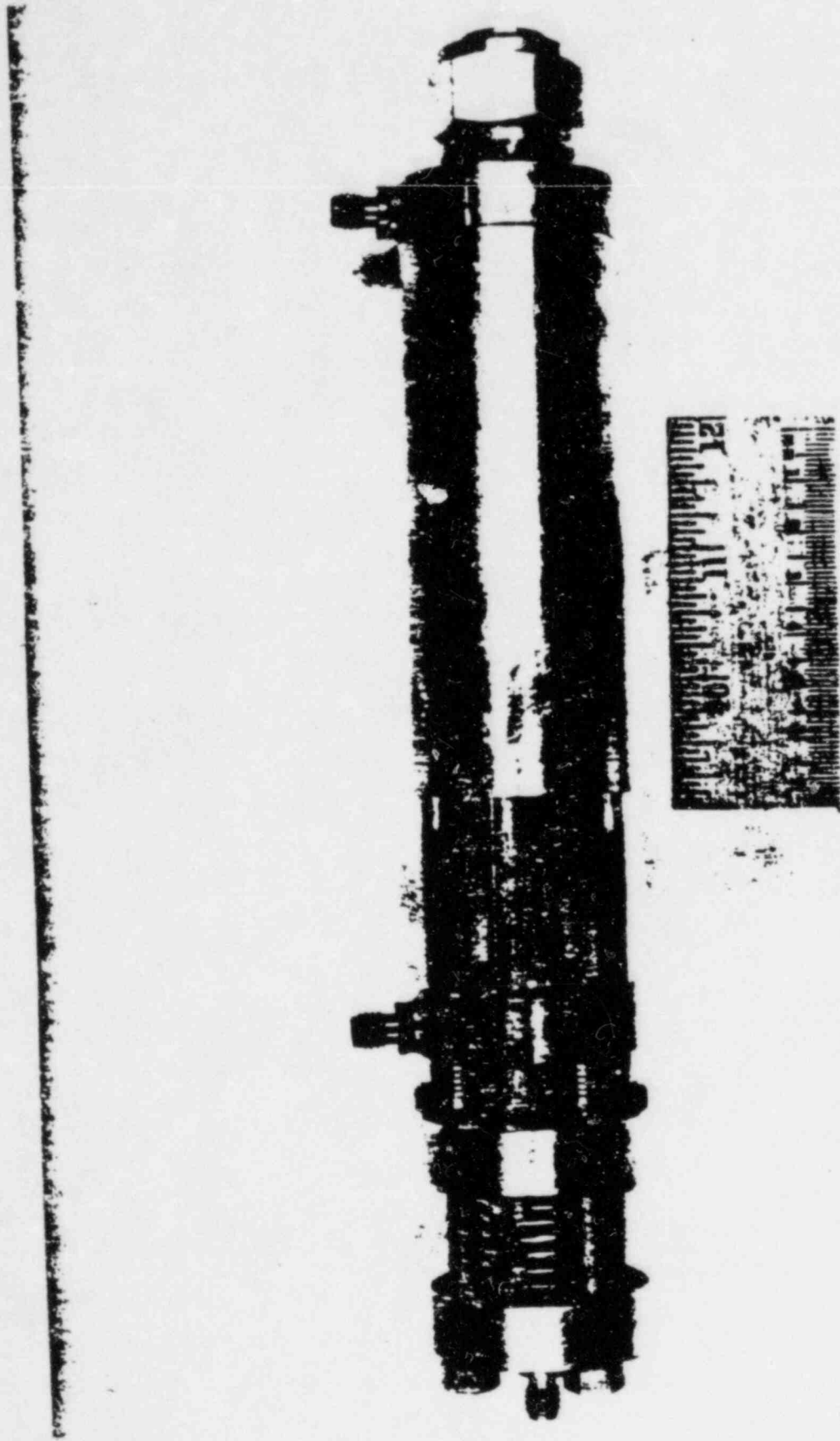


Figure 5.3. Repair Test Specimen Bellows Loading Assembly

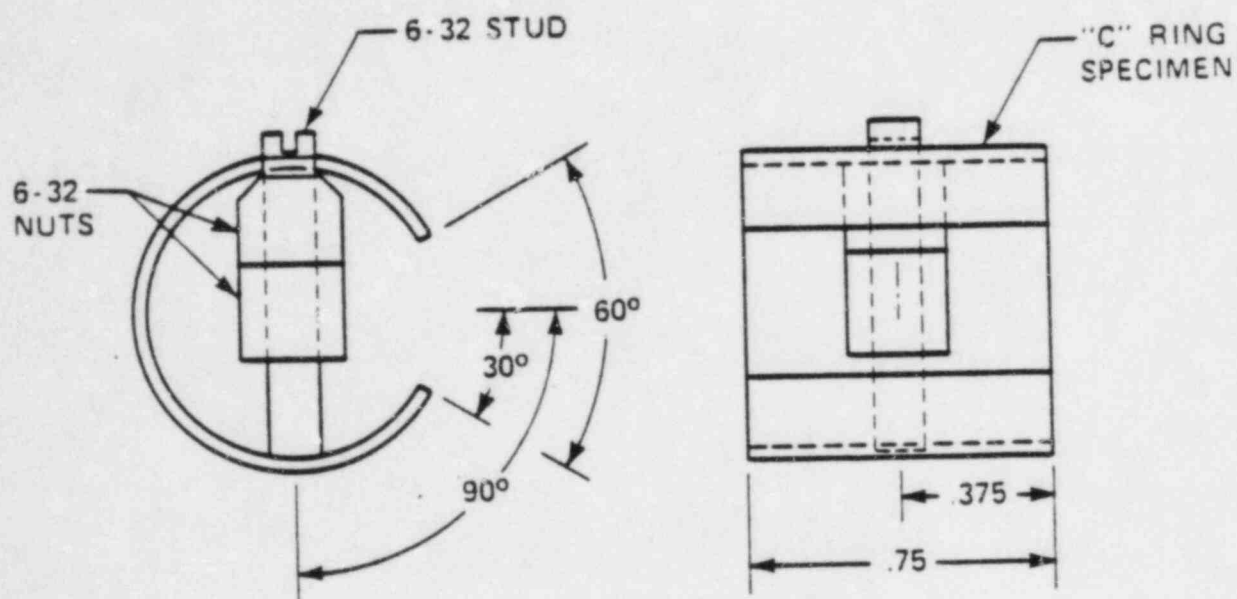


Figure 5-4
C-ring Specimen Configuration

TMI C-RINGS

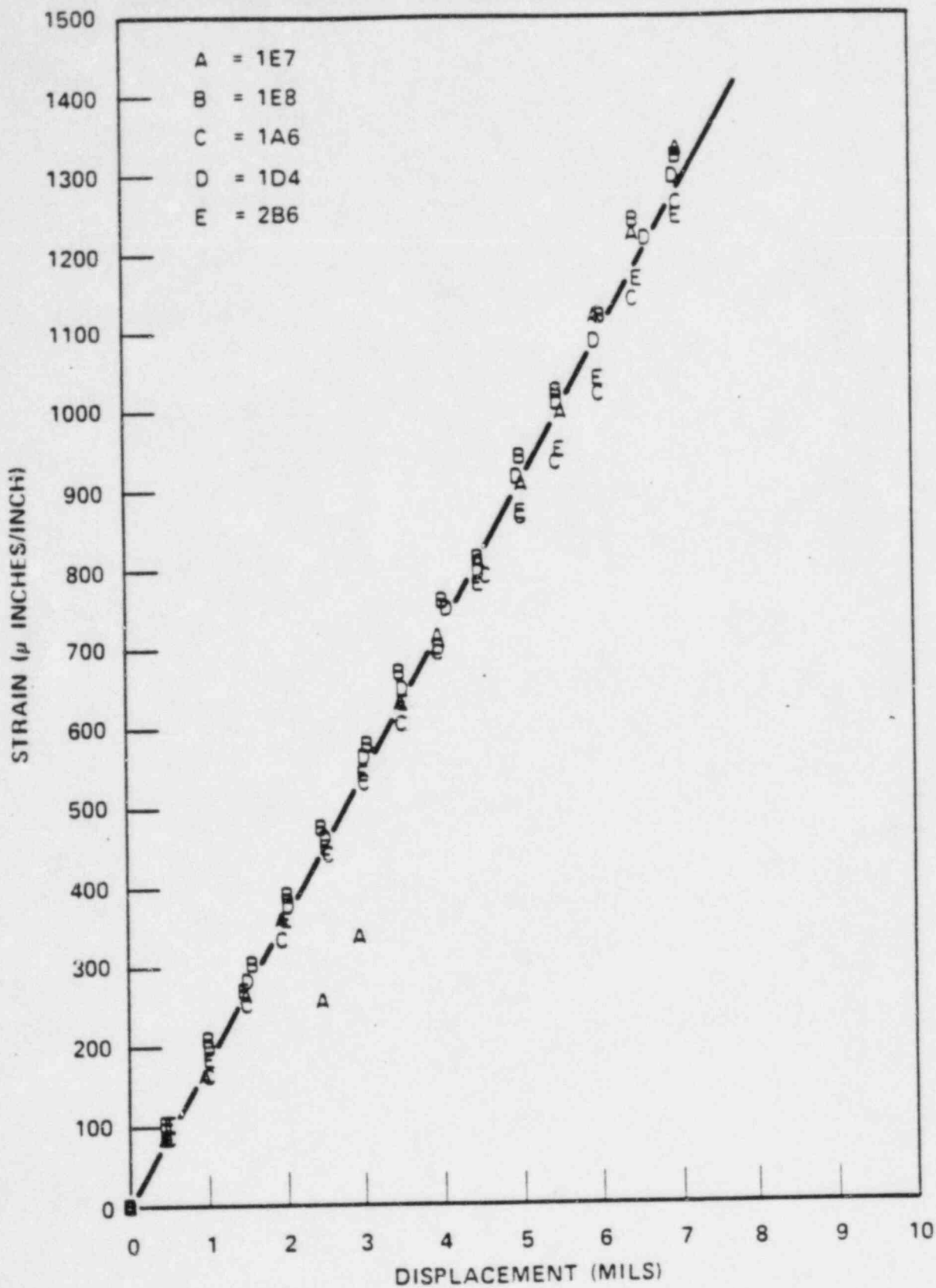


Figure 5-5
Strain Gage Results

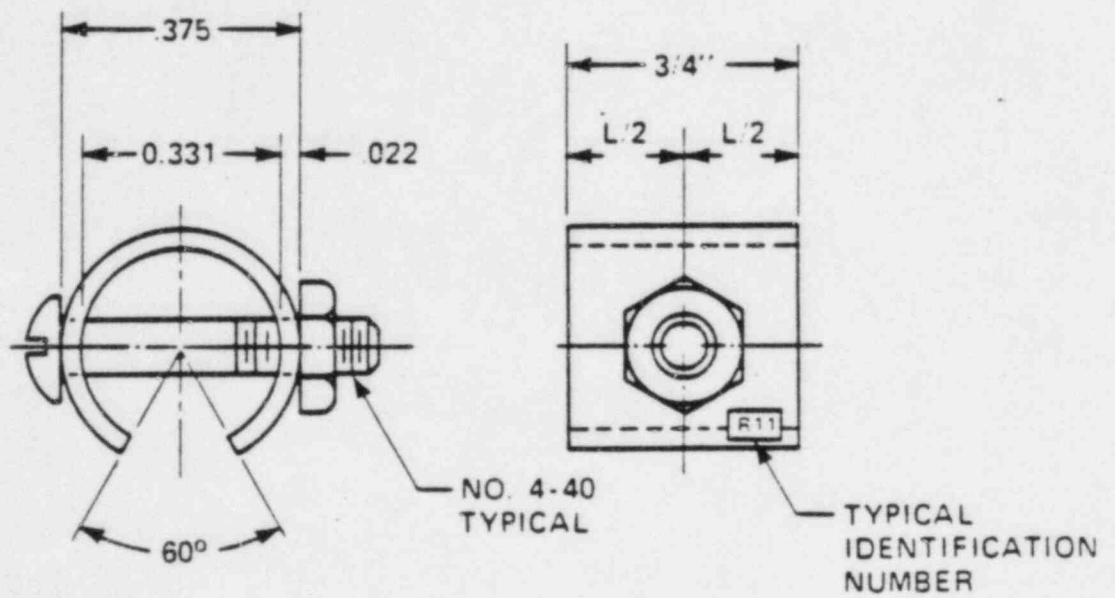


Figure 5-6
Zircaloy C-ring

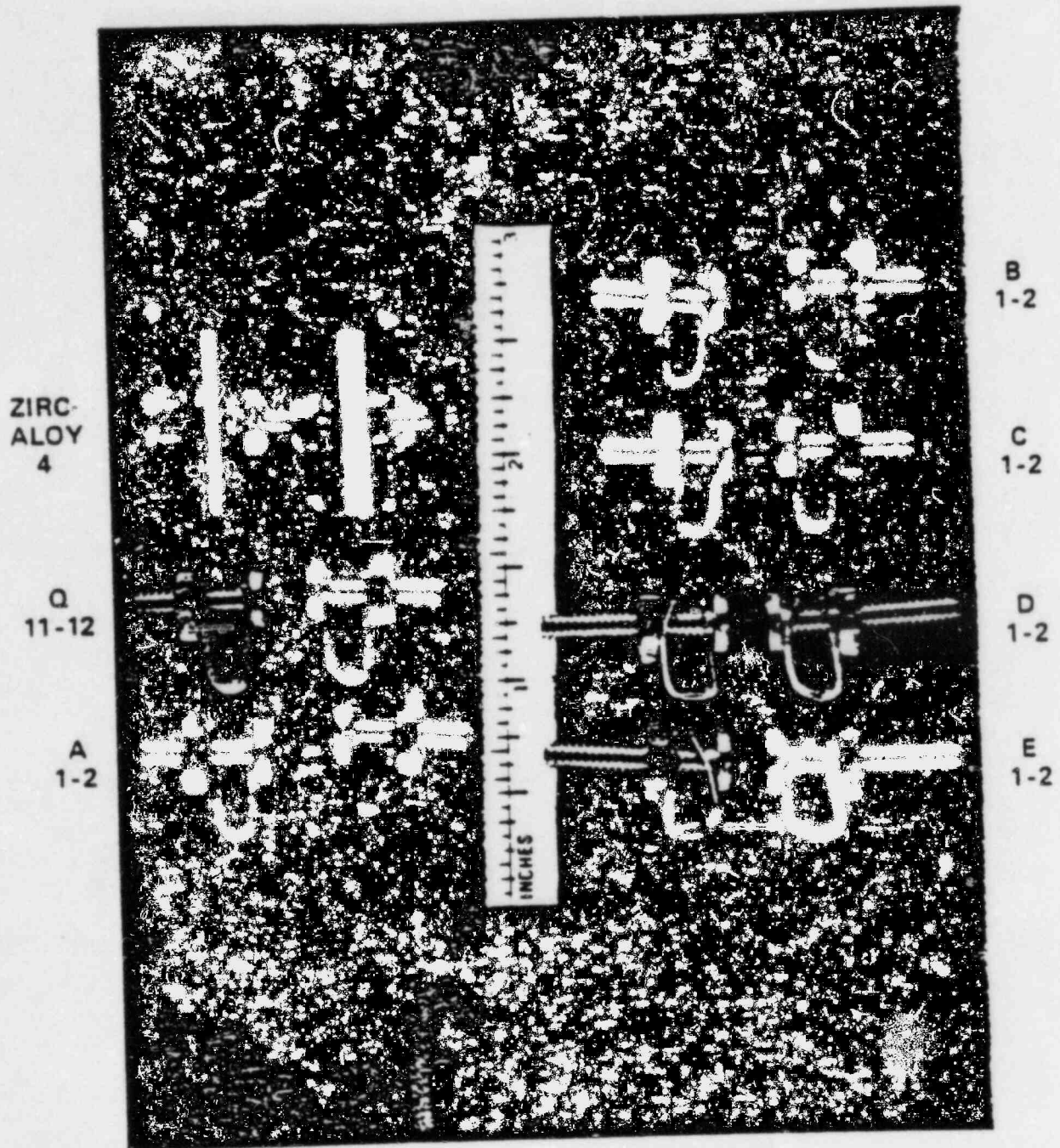


Figure 5.7. Core Material Specimens

Table 5-1
TMI-1 FULL SIZE TUBE IDENTIFICATION

<u>Tube</u>	<u>Section</u> ⁽¹⁾	<u>Heat No.</u>	<u>Defect Location</u> ⁽¹⁾
A24-94	19-5/16" - 25-7/16"	M2409	None
A13-63	11" - 20-9/16"	M2408	16"
B16-22	52" - 59"	M2800	None
A88-7	2" - 9-3/4"	M2560	6"
A16-69	6-1/2" to 12-1/4"	M2345	9"
A24-94	36" - 42"	M2409	None
B94-27	4-1/2" - 10-1/2"	M2869	None

(1) Dimensions from original top of tube in the OTSG.

Table 5-2
INCONEL 600 C-RING MATERIAL IDENTIFICATION

<u>C-ring Number</u>	<u>Tube</u>	<u>Location(1)</u>	<u>Slot(2) Angle</u>	<u>Heat</u>
1A1	A 88-7	9-3/4" - 12-1/4"	180°	M2560
1A2	A 88-7	9-3/4" - 12-1/4"	270°	M2560
1A3	A 88-7	9-3/4" - 12-1/4"	0°	M2560
1A4	B111-62	237-5/8" -240-5/8"	90°	M2560
1A5	B111-62	237-5/8" -240-5/8"	180°	M2560
1A6	B111-62	237-5/8" -240-5/8"	90°	M2560
1B1	A 24-94	25-7/16"- 30-13/16"	180°	M2409
1B2	A 24-94	25-7/16"- 30-13/16"	270°	M2409
1B3	A 24-94	25-7/16"- 30-13/16"	0°	M2409
1B4	A 24-94	25-7/16"- 30-13/16"	90°	M2409
1B5	A 24-94	25-7/16"- 30-13/16"	180°	M2409
1D1	B 94-27	18-1/2" - 24-1/4"	180°	M2869
2A1	A 13-63	20-9/16"- 23-9/16"	180°	M2408
2A2	A 13-63	20-9/16"- 23-9/16"	270°	M2408
2A4	A 13-63	38-1/8" - 42-1/8"	0°	M2408
2A5	A 13-63	38-1/8" - 42-1/8"	90°	M2408
2B1	B 16-22	59" - 64"	180°	M2800
2B2	B 16-22	59" - 64"	270°	M2800
2B3	B 16-22	59" - 64"	0°	M2800
2B4	B 16-22	59" - 64"	90°	M2800
2B5	B 16-22	59" - 64"	180°	M2800
2B6	B 16-22	59" - 64"	0°	M2800
1D5	B 34-19	10-1/2" - 14-1/2"	180°	M2869
1D6	B 34-19	10-1/2" - 14-1/2"	270°	M2869
1D7	B 34-19	10-1/2" - 14-1/2"	0°	M2869
1D8	B 34-19	10-1/2" - 14-1/2"	180°	M2869

(1) Dimensions from original top of tube in the OTSG.

(2) Location of C-ring cutout, per GPU-N reference angles.

Looking down tube, the angle increases clockwise with 0° at 6 o'clock, 90° at 9 o'clock, 180° at 12 o'clock, etc. The slot (cutout) occurs 180° from the resultant maximum stress on the C-ring.

Table 5-2 (Continued)

<u>C-ring Number</u>	<u>Tube</u>	<u>Location⁽¹⁾</u>	<u>Slot⁽²⁾ Angle</u>	<u>Heat</u>
2D1	A 16-69	2" - 6-1/2"	180°	M2345
2D2	A 16-69	2" - 6-1/2"	270°	M2345
2D3	A 16-69	2" - 6-1/2"	0°	M2345
1E1	Archive Material			M2320
1E2	Archive Material			M2320
1E3	Archive Material			M2320
1E4	Archive Material			M2320
1E5	Archive Material			M2320
1E6	Archive Material			M2320
1E7	Archive Material			M2320
P1A1 ⁽³⁾	A62-8	5" - 11"	0°	M2560
P1A2	A62-8	5" - 11"	90°	M2560
P1A3	A62-8	5" - 11"	180°	M2560
P1A4	A62-8	5" - 11"	270°	M2560
P1A5	A62-8	5" - 11"	0°	M2560
P2D1	A12-62	2" - 4-1/2"	0°	M2345
P2D2	A12-62	2" - 4-1/2"	90°	M2345
P2A1	A37-29	49-1/2" - 54-1/2"	0°	M2408
P2A2	A37-29	49-1/2" - 54-1/2"	90°	M2408
P2A3	A37-29	49-1/2" - 54-1/2"	180°	M2408
P2A4	A37-29	49-1/2" - 54-1/2"	270°	M2408
P2A5	A37-29	49-1/2" - 54-1/2"	0°	M2408
P1D1	B34-19	6-1/2" - 10-1/2"	0°	M2869
P1D2	B34-19	6-1/2" - 10-1/2"	90°	M2869
P1D3	B34-19	6-1/2" - 10-1/2"	180°	M2869
P1D4	B34-19	6-1/2" - 10-1/2"	270°	M2869
P1D5	B34-19	6-1/2" - 10-1/2"	0°	M2869

(3) Specimens with a "P" prefix were received treated with ^{a precoat} and exposed to debris from the explosive expansion.

Table 5.3

Compositions of Alloys Used to Prepare Mini-U-Bends
(values in weight %)

Alloy	Element													
	C	Si	Mn	S	Ni	Cr	Fe	Ti	Al	Nb + Ta	P	Cu	Co	Other
Inconel X-750	0.04	0.03	<0.01	0.004	72.57	15.60	7.10	2.60	0.70	1.01	-	0.01	0.03	-
17-4 pH	0.038	0.86	0.40	0.003	4.30	15.79	Bal.	0.01	0.02	0.32	0.31	3.29	0.08	0.23 Mo 0.025 N
410	0.11	0.30	0.44	0.009	0.40	12.48	Bal.	-	-	-	0.017	-	-	0.24 Mo
304	0.061	0.60	1.60	0.02	9.20	18.45	Bal.	-	-	-	0.031	0.32	0.13	0.42 Mo 0.10 N
308L*	0.03	1.0	2.0	0.03	10.0 to 12.0	19.0 to 21.0	Bal.	-	-	-	0.045	-	-	-
Inconel 600	0.06	0.22	0.17	0.007	76.05	15.40	7.92	-	-	-	-	0.15	-	-
Inconel 82	0.02	0.16	3.17	0.004	72.32	19.04	2.25	0.35	-	2.51	-	0.14	-	-

* approximate composition

Table 5-4
ALLOY SUPPLIER, HEAT NO., AND FORM

<u>Alloy</u>	<u>Supplier</u>	Heat No. or Heat Treatment <u>Code</u>	<u>Form</u>
Inconel K-750	Universal Cyclops Corp. Pittsburgh, Pa.	Q902	Plug machined from bar stock
17-4 pH	JOSLYN Stainless Steel, Fort Wayne, Inc.	Heat No. 80581	Bar stock (2.5" dia)
410	Carpenter Technology, Reading Pa.	Heat No. 829985	1" plate
304	Jessop Steel Co., Washington, Pa.	Heat No. 30653	Plate
308L	—	—	Wire
Inconel 600	Williams and Co., Pittsburgh, Pa.	Heat No. NX9349	Plate
Inconel 82	Huntington Alloys, Inc., Huntington, West Va.	Heat No. 72980	Wire
Zircaloy 4	Data Proprietary - Stress annealed similar to B+W tubing.		

Table 5.5

Alloy Heat Treatment and Mechanical Properties

Alloy	Heat Treatment	Rockwell Hardness	Yield Strength ksi	Tensile Strength ksi	Elong. in 2" %
Inconel X-750	1800°F/0.5 h + 1350°F/8 h + 1150°F/10 h	C-38.4			
17-4 pH	1900°F/1 h + 1100°F/4 h*	-			
410	1600°F/0.5 h + furnace cool to 1100°F**	-			
304	As Received	-	41.1	84.0	66
308L	1150/7 h***	-	-	-	-
Inconel 600	As Received (cold rolled, annealed and pickled)	B-80.0	47.0	91.0	45
inconel 82	-	-	-	-	-

* Westinghouse anneals 3689 and 3690

** Westinghouse anneal 3688

*** Westinghouse anneal 3687

Table 5-6
 ALLOYS AND U-BEND CODING

<u>Alloy</u>	<u>Coding of Mini-U-Bends</u>
Inconel X-750	Q-11 Q-12
17-4 pH	A-1 A-2
410	B-1 B-2
304 (1150°F/7 h)	C-1 C-2
308L Filler Metal on 304 (as required)	D-1 D-2
Inconel 82 Filler Metal on Inconel 600	E-1 E-2

Table 5-7
LONG TERM CORROSION TEST SPECIFICATIONS

	<u>Test No. 1</u>	<u>Test No. 2</u>
Boron (H_3BO_3)	2350 - 100 ppm B	2350 - 100 ppm B
Lithium (LiOH)	2.5 - 0.7 ppm Li	2.5 - 0.7 ppm Li
Thiosulfate ($Na_2S_2O_3$)*	0.5 - .15 ppm SO_4	-----
Sulfate (Na_2SO_4)	-----	.05 - .15 ppm SO_4
Chloride (NaCl)	0.5 - .15 ppm Cl	.05 - .15 ppm Cl
Fluoride (NaF)	0.5 - .15 ppm F	.05 - .15 ppm F
pH	5.0 - 7.5	5.0 - 7.5
Hydrogen	15-40 cc/kg	15-40 cc/kg
Hydrazine (N_2H_4)	2-10 ppm	2-10 ppm
Oxygen	< 10 ppb	< 10 ppb

*Specified as sulfate equivalent

<u>CYCLE</u>	<u>BORON (ppm)</u>	<u>LITHIUM (ppm)</u>
Preconditioning	2350 \pm 50	2.2 - 2.5
KFT	2350 \pm 50	2.2 - 2.5
First Cycle	1200 \pm 20	2.2 - 2.5
Second Cycle	1000 \pm 20	1.7 - 2.0
Third Cycle	500 \pm 10	1.0 - 1.3
Fourth Cycle	100 \pm 10	0.7 - 1.0
Fifth Cycle	100 \pm 10	0.7 - 1.0
Sixth Cycle (which ends the test)	100 \pm 10	0.7 - 1.0

6.0 OPERATING HISTORY

The operating parameters for the long term corrosion and peroxide cleaning experiments were specified by GPU-N to simulate expected operating parameters of the TMI-1 steam generators. The experiments consist of maintaining pressurized flow of solution through the specimens while varying temperature and the applied load on the full size specimens.

Two autoclaves have been used for the LTCT program. Autoclave 2 contained specimens exposed to sulfate chemistry and Autoclave 1 contained specimens exposed to thiosulfate chemistry. Autoclaves 3 and 4 were operated in series for the peroxide experiment and have been converted into once-through long term corrosion apparatus for exposure of specimens exposed to the 500 hour peroxide treatment.

6.1. Test Parameter Recording and Control

6.1.1 Temperature - Proportional type controllers regulated current to autoclave heaters. The indicating thermocouple was placed in a well inserted through the head into the autoclave water. The control thermocouple was in contact with the autoclave OD within the space envelope generated by the band heaters.

Typical temperature variation was $\pm 5^{\circ}\text{F}$. Temperatures were recorded daily.

6.1.2 Pressure - Specimen ID and OD (autoclave) pressures were equal due to leaks in the specimen package. The pressure was developed and maintained with a high pressure diaphragm pump and a mechanical back pressure regulator. The test system pressure was maintained ± 20 psig.

The bellows gas pressure used to maintain specimen load was controlled to within ± 20 psig which is equivalent to about ± 10 lb on the specimens. Since the response of both specimens in an autoclave was slightly different, due to slack in the loading system, total specimen load may have varied ± 10 percent from specification.

6.1.3 Flow Rate

Solution flow rates were typically 100 ± 50 cc/hr. Some deviations occurred during temperature cycling; these were compensated for by adjusting the pumping rates where possible.

6.1.4 Record of Test Parameters

Monthly tabulations of recorded temperatures, pressures and flowrates for Tests 1 and 2 are presented in Appendix 10.5. This appendix also contains plots of the measured temperatures and pressures for these tests.

6.2 Loop Cleaning and Preconditioning

Upon the completion of construction of each autoclave loop system, a period of cleaning and sulfur preconditioning was undertaken prior to LTCT operations. The pre-operational system flushing and cleanup was accomplished by pumping high purity demineralized water from the MUT through the system with the autoclave at 600°F. During the cleanup, test samples were not placed in the autoclave with the result that the flushing process also cleaned the internal autoclave surfaces. The effectiveness of the hot water flush was determined by evaluating the results of periodic conductivity and chloride ion analyses.

The following values are typical of those found for the makeup water used during the flushing process: conductivity < 0.5 μmho , $\text{Cl}^- < 1$ ppb, $\text{F}^- < 1$ ppb, $\text{SO}_4 = 1$ ppb. Flushing was terminated on Loop No. 2 when a Cl^- concentration of 0.2 ppm and conductivity of 6 μmho was achieved. When flushing was terminated on Loop No 1 the following concentrations in the loop effluent were measured: $\text{F}^- = 1$ ppb, $\text{Cl}^- = 4$ ppb, $\text{SO}_4^{2-} = 9$ ppb.

During preconditioning, a length of stainless steel tubing was placed in the autoclave and fastened to inlet and outlet ports on the autoclave head. Preconditioning solution, therefore, flowed through this tubing and did not contact the autoclave internal surfaces. The "preconditioned" stainless tubing was subsequently used to prepare the sample train used in the respective LTCT exposures.

Both autoclave loops were preconditioned at 600°F with solution identical to that used in the Test 2 HFT cycles. Flow of preconditioning solution was maintained until an effluent SO_4^{2-} concentration \geq 90 percent of the influent value was achieved. Three to five days was required to precondition test systems.

6.3 Autoclave Loading

Test specimen identification for each autoclave is shown in Table 6-1. All C-rings and U-bends were placed in cans in series flow with the full size tubes. A typical package of specimens is shown in Figure 6-1.

The total load applied to a tube specimen is the summation of the load applied by the bellows and the load resulting from the pressure differential across the tube wall. Since it was originally intended to operate each test system with a ΔP across the specimen walls, procedures were written which required that the bellows pressure be adjusted to compensate for changes in pressure across the tubing wall during thermal transients and, therefore, would maintain the sample load constant. However, during heatup it was noted that the primary to secondary ΔP decreased more rapidly than anticipated and eventually became zero due to primary to secondary system leakage through defects in the test specimens. During heatup the next effect of through-wall leakage and thermal expansion of the secondary fluid was the gradual elimination of the ΔP and establishment of a single phase (solid) secondary system. Until the secondary system was solid, this required that the bellows pressure be increased to maintain a constant sample load. But once the system was solid, specimen load was controlled solely by bellows load. Controlling specimen load during cooldown became so experimentally difficult that it required almost continual monitoring and control. This resulted from the fact that the leak rate through the tube defect was variable and insufficient to compensate for the contraction of water during cooldown.

A modification was therefore made to each of the four test systems which simplified the control of specimen load. The modification consisted of installation of a bleed line from the primary system to the autoclave or

secondary side. This line permitted the primary solution to fill the autoclave and maintain a solid secondary system at the same pressure as the primary system throughout the entire experiment. Elimination of the ΔP across the tube permitted the specimen load to be controlled by only the bellows loading system.

6.4 Long Term Corrosion Experiments

The two autoclaves were operated as long term corrosion experiments 1 and 2. The experiments consist of a hot functional test (HFT) of about one month duration followed by a series of six two months operational cycles with varying solution chemistry. During each phase the system temperature and full size specimen loads were varied to simulate actual steam generator operating conditions.

The detailed test sequences for the HFT and operating cycles are presented in Appendix 10.1 and in 10.2, respectively. During heat up and while at temperature the full size specimen loads were maintained at 500 lb. At the beginning of each cool down to ambient, the load was increased to 1100 lbs and held there until the final temperature was reached. The load was then reduced to 500 lbs., except at the end of the cycle where it was reduced to 0.

Figure 6-2 is a stylized curve of the temperature vs. time regime for the HFT cycle of the GPU-N lead tests, and as such is an idealized representation of the cycle for both autoclaves 1 (Lead Test 1) and 2 (Lead Test 2). Figure 6-3 is a also a stylized curve depicting the ideal thermal profile for all of the subsequent operating cycles of both GPU-N Lead Tests.

The departure of the temperature from the ideal curve was minimal in the ramping, cycling, and steady state stages of the HFT and operating cycles.

Computer generated curves and tables for the actual operating parameters of Tests 1 and 2 through the HFT and first two operational cycles are presented in Appendix 10.5.

Water samples were withdrawn from the make-up tank and autoclave effluent after each new batch of make-up water was added (~3 weeks) and two weeks thereafter.

6.5 Autoclave Operational Variations

Both autoclaves operated through the first cycle with little deviation from specifications. One general variation was the adjustment of the test sequences to conform to a five day work week. For example, Step 6 of the operational sequence (see Appendix 10.2) requires 10 continuous days of temperature cycles. These cycles were interrupted during week ends. The test temperature at the end of a work week was maintained through the weekend. At the beginning of the next work week, cycling was reinitiated as prescribed in the test sequence.

Test 2 was started before a technique was developed for measuring specimen load from bellows pressure. During the HFT it is estimated that loads were actually 200 lbs low in the specimen. Also, for this autoclave one bellows failed during the pressure increase proceeding the cooldown to ambient for both the HFT and Cycle 1. After each bellows failure, the system was opened, the bellows replaced and the remainder of the test continued according to the test specification. The next effect of the bellows failure was loss of load during the cooldown from 600 to 140°F. The bellows failure did not occur until most of the load increase was achieved with the result that the tubes were subjected to most (but not all) of the high stress at 600°F. The effect of this deviation from the test specification on the tube integrity can not be assessed.

Examination of the bellows indicated ID initiated stress corrosion cracking as the cause of the failure. Failure was, therefore, from the gas side and not a result of exposure to autoclave water. Residual moisture and chloride contamination were suspected in the failed bellows. All bellows internal surfaces were subsequently washed in high purity water and thoroughly dried before use.

Minor deviations from specifications are recorded in daily record log books on permanent file in the Westinghouse Research Center Remote Metallographic Laboratory.

6.6 Chemistry Monitoring During the HFT, First and Second Operating Cycles of Lead Test 1

During the performance of the various test cycles, analyses of MUT solutions and effluent solutions, which had passed through or over the test specimens, were routinely performed. The intent was to control MUT chemical concentrations within specified limits and monitor effluent solution levels to determine what changes may have resulted from exposure to the test specimens. The results of these analyses would provide documentation of the chemical composition of the test solutions during each of the exposure periods.

MUT solutions were prepared as described in Appendix 10.3 (Section 10.3.2) from concentrated stock solutions which in turn were prepared as described in Appendix 10.3 (Section 10.3.1). MUT solutions were always prepared from stock solutions whose concentrations had been verified by chemical analyses. However, due to the time delay between sampling and analyses of MUT solutions, no adjustments were made in make-up tank compositions based on the results of chemical analyses of MUT samples. In most cases, make-up tank solutions were completely consumed prior to receipt of the results of chemical analyses on samples withdrawn shortly after their preparation.

The analytical chemistry results for samples collected from Lead Test 1 are given in Tables 6-2, 6-3 and 6-4 for the HFT, first and second operating cycles, respectively. The data in these tables shown that no difficulty was encountered in maintaining either MUT pH or dissolved oxygen within control limits. Minor deviations in lithium and boron target concentrations were observed during both cycle 1 and cycle 2. These variations may have arisen from operational considerations between and during cycles.

Between each operational cycle, the MUTs were backflushed with deionized water and drained prior to filling with freshly prepared MUT solutions. If the MUT had been incompletely drained following the flushing operation, the new MUT

change would be diluted by any unremoved flush water. The location of the drain valve on the MUT (in the side rather than the bottom of the tank) makes incomplete removal of flush water a probable event resulting in a decrease in both lithium and boron in some cases.

Likewise there was at least one operational variation which could have resulted in an increase in chemical concentrations of these species. After preparation, each MUT solution is sparged with inert gas to remove dissolved oxygen. If the sparging rate or length of sparging time varied between MUT preparations, concentration of MUT nonvolatile species may have resulted by loss of water vapor, carried off with the sparging gas. Either of these two events or some combination of these events may have occurred and caused the observed variations in targeted MUT concentrations.

Minor difficulties in control of boron concentrations became apparent as the concentration and the corresponding control band for boron decreased. The relatively narrow control band for boron established at the lower nominal boron concentrations appears to be an unreasonably tight control band in the small volume test systems employed in this program. Broadening of this band should be considered in subsequent cycles.

Fluoride, chloride and thiosulfate were to be controlled at low ppb levels in this test. Extreme difficulty was encountered with control of the MUT fluoride concentrations. Experience in both Lead Test 1 and 2 showed that, although required volumes of the analytically verified fluoride stock solution were added to the MUT, low resulting fluoride concentrations were observed. This was attributed to adsorption of fluoride on the walls of the polyethylene holding tank. The practice of adding F^- directly to the stainless steel MUT during transfer of solution from the polyethylene holding tank was adopted to attempt to minimize adsorption, but this practice has proved inadequate in increasing MUT fluoride levels. Adsorption of fluoride on the stainless steel MUT walls is also thought to be occurring.

Some difficulty was also encountered in controlling chloride at the desired MUT levels. Although chloride levels in the MUT were within the targeted control band during the HFT cycle of Test 2, MUT chloride concentrations during the HFT and second operating cycle were frequently a factor of two high.

Although the targeted thiosulfate level in this test (0.0585 ppm) was only slightly above the limit of detection of thiosulfate by the ion chromatographic analysis method, no thiosulfate was detected in any MUT or effluent samples. Although sulfate was routinely detected in effluent samples, the level of sulfate in these samples decreased with time during each cycle. It can not be determined whether the observed sulfate was derived from thiosulfate or was simply a result of specimen (or specimen train) sulfate contamination.

Initial effluent samples were extremely high in fluoride, chloride and sulfate in each test cycle. Values for these species did decrease with continued exposure to fresh MUT solutions and effluent concentrations gradually approached those of the MUT solutions. This is attributed to contamination of the specimens and specimen trains during post exposure visual examinations. This contamination occurred despite strict compliance with operational procedures and techniques designed to minimize contamination. The highest effluent levels were observed in the initial effluent sample taken during the HFT cycle. Since the full length tube specimens received no pre-test rinsing and since some specimens received ^{a precoat} treatment, this high initial effluent values are not unreasonable.

Overall deviations from targeted concentrations have not been great and are not expected to have a major impact on tube corrosion.

6.7 Chemistry Monitoring During the HFT, First and Second Operating Cycles of Lead Test 2

Tables 6-5, 6-6 and 6-7 are tabulations of the analytical chemistry results for water samples withdrawn during HFT, first and second operating cycles respectively of Lead Test 2. As in Test 1 (Section 6.6) some difficulty was encountered in maintaining Li^+ , B, Cl^- , F^- and SO_4^{2-} MUT concentrations within the targeted MUT range for each of these species. The discussion found in Section 6.6 is also pertinent for the results of this test. The high initial effluent values for F^- , Cl^- , and SO_4^{2-} observed early in each cycle are attributed to wash-off of these species from specimen and specimen container surfaces.

6.8 Hydrogen Peroxide Experiment

The hydrogen peroxide experiment was a 500 hour experiment designed to simulate the proposed TMI-1 steam generator cleaning procedures. Solutions containing hydrogen peroxide were passed through a series of full size tube specimens and cans of U-bends and C-rings. The recirculating system was regularly replenished with H_2O_2 to maintain the peroxide concentration in the specified control range.

Nominal operating parameter specifications for this experiment were:

Temperature , 130°F
Pressure , 10 psig (from make-up tank overpressure)
Flow rate , 2 gallons/hr
pH , 8.0 - 8.2
Boron , 2350 ppm
Lithium , 1.5-2.2 ppm
 H_2O_2 level , 15 - 20 ppm
Full size specimen load , 500 lbs.

6.8.1 Loop Cleaning and Preconditioning - Cleanup and preconditioning of the loops used in the peroxide cleaning procedure was accomplished as described in Section 6.2. Each autoclave assembly was flushed with high purity deionized water, with the plumbing in the once-through mode. Water flushing of the first peroxide loop autoclave (Loop 3) commenced January 28, 1983 and was completed on February 3, 1983; the flushing of the second peroxide loop autoclave (Loop 4) began on February 7, 1983 and was completed on February 9, 1983. The high purity water cleanup of the autoclave systems was followed by a sulfate preconditioning with the autoclave plumbing remaining in the individual, once through configuration.

The primary function of the sulfate preconditioning was to attain a stable system "steady state", relative to the sulfate, in which the sulfate concentration of the effluent is at or near the sulfate of the influent solution. This was accomplished by exposing the tubing and system, exclusive of the GPU-N specimens, to a sulfate solution and analyzing the effluent. The

sulfate analytical results for Loops 3 and 4 in the once-through cleaning and flushing operation are given in Tables 6-8 and 6-9, respectively.

Since there was interest in monitoring the loop sulfate level during the hydrogen peroxide experiment, care was taken during the clean-up and preconditioning of the loop systems to establish baseline sulfate values. Tables 6-8 and 6-9 present the results of sulfate analyses obtained by ion chromatography for samples withdrawn from the loops during these operations. Sulfate preconditioning of Loop 3 was completed on February 9. The preconditioning of Loop 4 were completed on February 17.

6.8.2 Loop Operation with Peroxide Additions - After preconditioning, Loops 3 and 4 were combined as shown in Figure 4-3 to form the closed loop system used during the peroxide cleaning. The specimens, as identified in Table 6-1, were placed in Autoclaves 3 and 4 and the MUT filled with 50 l of a solution containing 2350 ppm B as boric acid and 2.1 ppm lithium as lithium hydroxide. After the MUT was sampled to determine the baseline SO_4^{2-} level (See Table 6-13), one liter of MUT solution was flushed through the system (specimens remained by-passed) and removed via the effluent sampling line. A sample of this initial flush solution was also retained for analysis (See Table 6-13).

Additions of ammonium hydroxide and sodium sulfate solutions were made to adjust the MUT pH to 8.2 and increase the sulfate concentration to a value comparable to that used during loop preconditioning. These additions were also made with the test specimens by-passed.

Because a "primary-to-secondary" leak at the tube collar weld was detected during the leak checking (which is part of the specimen assembly procedure) a drain line was connected from autoclave 3 to the MUT. This drain line prohibited the autoclave pressure from gradually increasing to that of the primary system and, thereby, significantly simplified operation of the specimen loading fixture by eliminating the need to frequently adjust gas pressure in the bellows. This drain line remained open to the MUT throughout the entire peroxide cleaning procedure.

The H_2O_2 injections into the circulating system were started by discrete manual introduction at hourly intervals. Later, an automatic peroxide injector was added to the system to allow routine metered peroxide addition to the system.

A summary of the changes made to the apparatus for increased efficiency or because of unforeseen circumstances is given in Table 6-10.

The average daily peroxide concentration of the solution in the make-up tank, as well as the pH of this solution, is reported in Table 6-11; the daily peroxide usage is tabulated in Table 6-12. All of the pertinent peroxide data listed in Tables 6-11 and 6-12 are plotted in Figures 6-4, 6-5 and 6-6.

It should be noted that in order to maintain the peroxide concentration in the make-up tank (MUT) within the selected limits, the peroxide additions (or deletions) were both continuous and discrete; i.e., the addition of the peroxide was generally accomplished with the automatic injector system, with additional manual injections if the MUT peroxide concentration was too low. Conversely, if the MUT peroxide concentration began to increase over the target value, the injector was turned off for a predetermined length of time. Because of this distinction, the average rate of peroxide addition was determined by dividing the weight of peroxide added in a given period (in all but the first and last cases, one day) by the number of hours in that period.

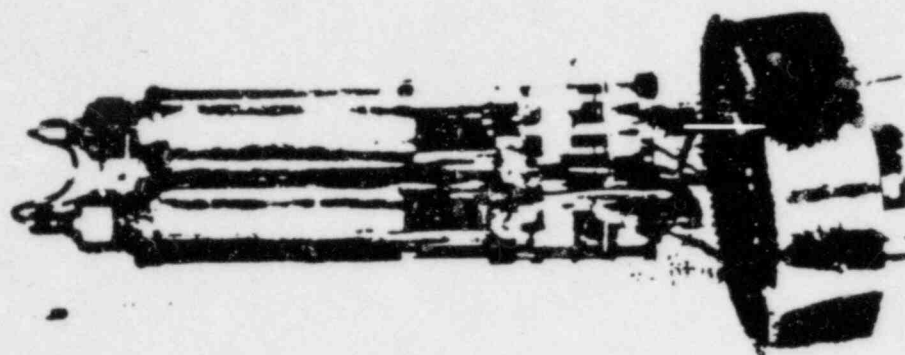
The scatter in the data for the weight of peroxide added (concentration) and the average weight of addition for the first 90 hours can be attributed to the learning process of the operators. This learning process is graphically illustrated in Figure 6-4: as the skill of the operators increased, the range of values of the average daily MUT peroxide concentration decreased. After 150 hours of operation, there was a gradual decrease in the amount (and average rate) of peroxide addition needed to maintain a 15 ppm hydrogen peroxide concentration in the MUT (Figure 6-5). This decrease in the amount of H_2O_2 which was added can most probably be attributed to the gradual decrease in volume of solution in the loop caused by sampling.

6.8.3 Chemistry Monitoring During the Peroxide Experiment - During the entire 500 hour peroxide exposure control of chemistry was very good. Figure 6-6 shows that the system pH remained essentially constant at pH 8.2. Boron and lithium concentrations showed some minor variation which is presumed to be due to the normal fluctuation in values resulting from the analysis of these species and does not reflect any effect of peroxide additions.

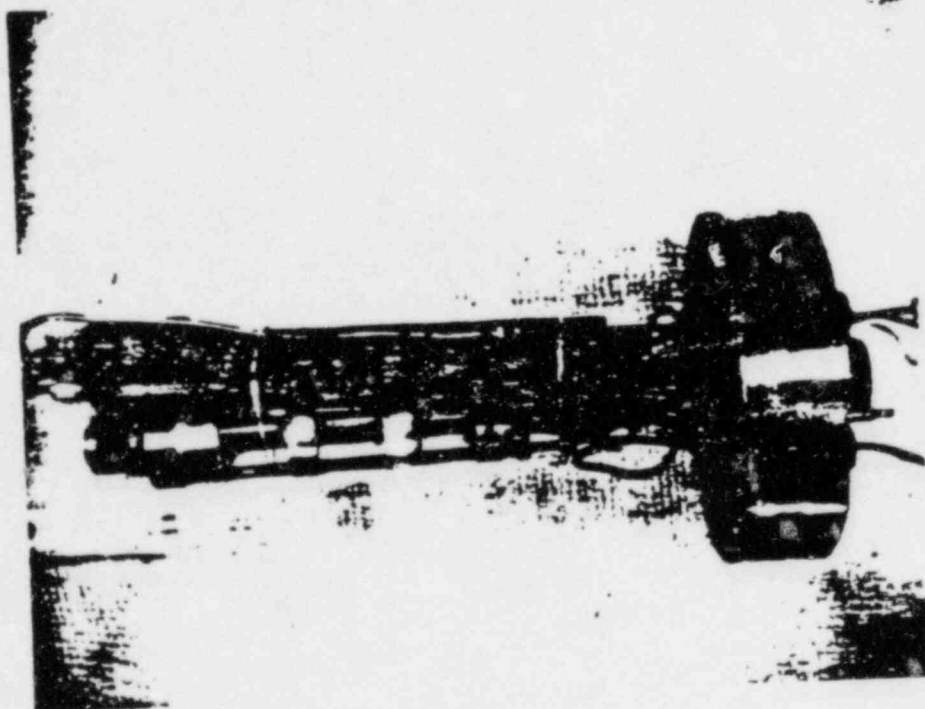
Peroxide concentrations initially showed some variation from the 15-20 ppm specification due to the inadequacy of manual additions to compensate for consumption rates. Following installation of the peroxide injection system, the observed spread in peroxide concentration values was narrowed significantly (See Figure 6-4).

The analytical chemistry data obtained by analysis of the solutions withdrawn from the loop during the peroxide exposures are presented in Table 6-13. During the first three days of exposure to peroxide containing solutions, the sulfate concentration in the effluent solutions gradually increased. Although the refilling of the MUT with fresh solution on the fourth day of testing (which was necessary due to solution loss resulting from the events documented in Table 6-10) caused a temporary reduction in the effluent sulfate concentrations (simply by dilution) effluent sulfate values continued to increase through the first eight days of testing before stabilizing at ~ 300 ppb after 200 hours of exposure. Although the observed increase in effluent sulfate may have been due to oxidation of lower oxidation state sulfur containing species on tube surface or to the release of sulfate from the network of intergranular attack comprising the tube defects, the possibility that the observed increase in effluent sulfate was due to contamination during the preparation of C-rings and U-bends or during assembly of the full length tube specimens can not be discounted.

The inaccuracies involved in estimating the volumes of solution lost during the unexpected system leaks of February 25 and 26 (See Table 6-10) make any attempt at a material balance for sulfate, at best, crude. Nevertheless, material balance calculations were made which show that approximately 17 mg of SO_4^{2-} , or approximately 7 mg of S, in excess of that intentionally added to the loop in MUT solutions, was moved from sample train assemblies during the peroxide exposures.



TEST 3



TEST 4

FIGURE 6.1 - Typical Specimen Packages, Test 3 Contains Two "Repair" Type Specimens and Test 4 Contains One "Lead" Type Specimen and Cans of C.Rings and U-Bends.

Curve 7436.73-A

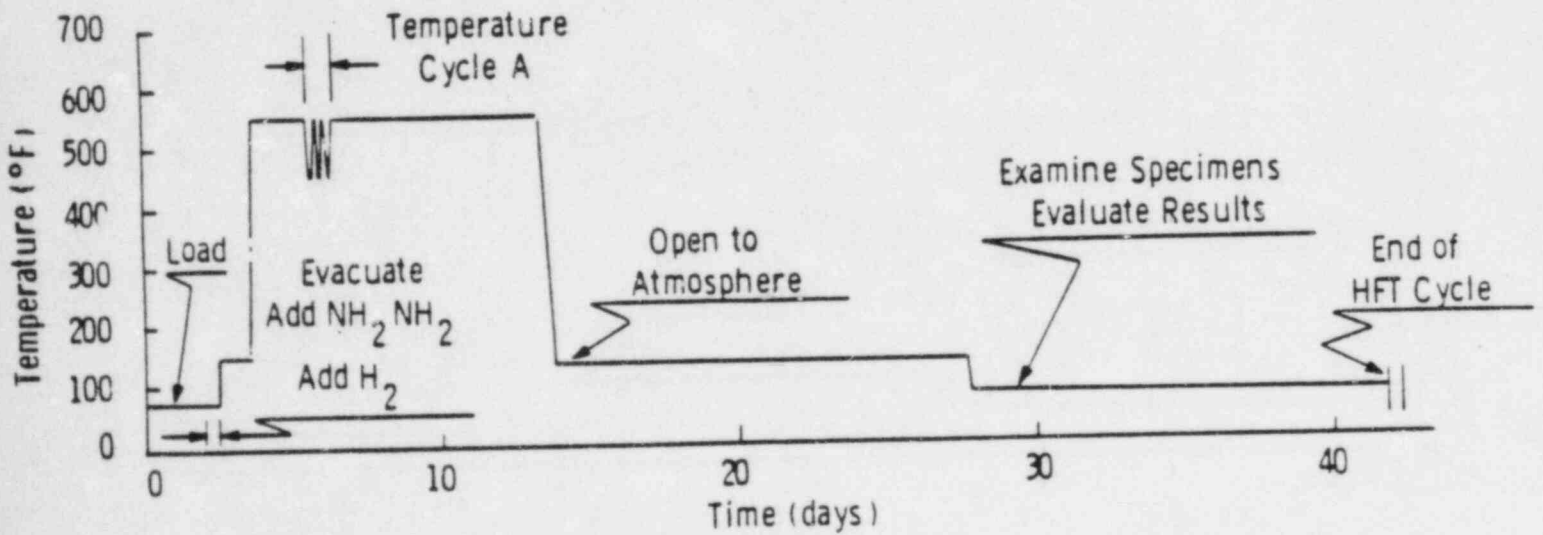
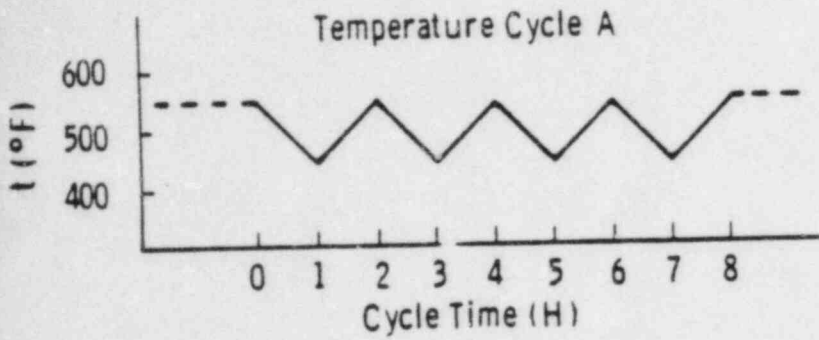


Figure 6-2 Stylized HFT Curve

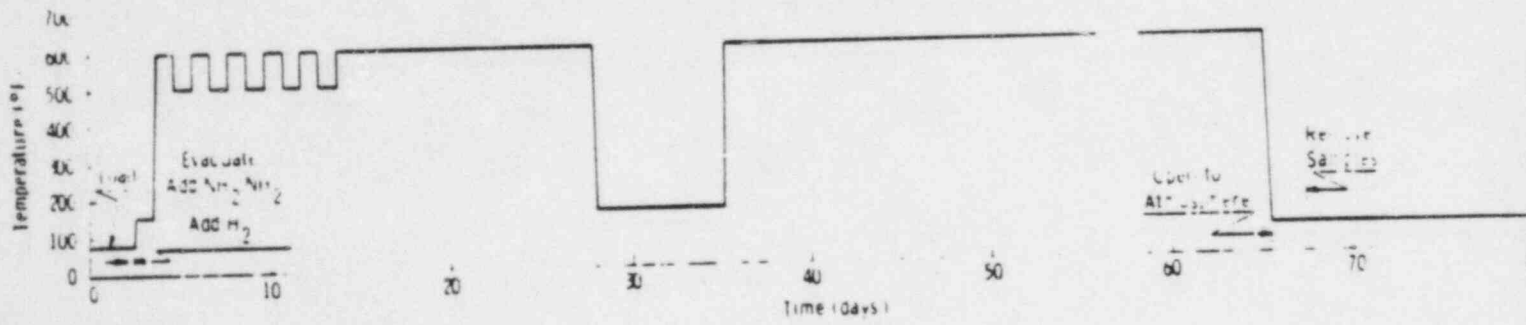


Figure 6-3 Stylized Lead Test Cycle

GPU PEROXIDE EXPERIMENT

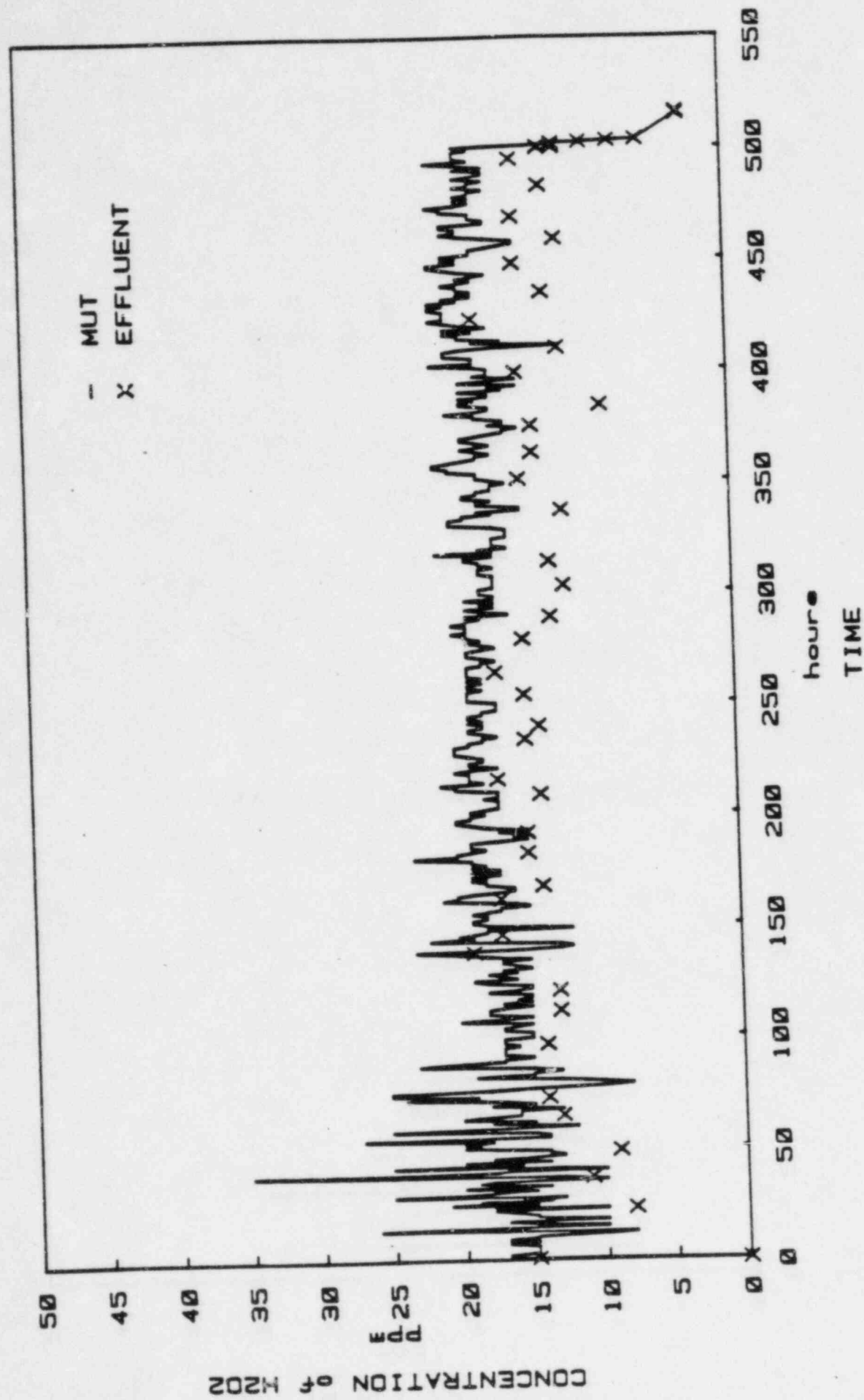


FIGURE 6-4 H₂O₂ CONCENTRATION VALUES

GPU PEROXIDE EXPERIMENT

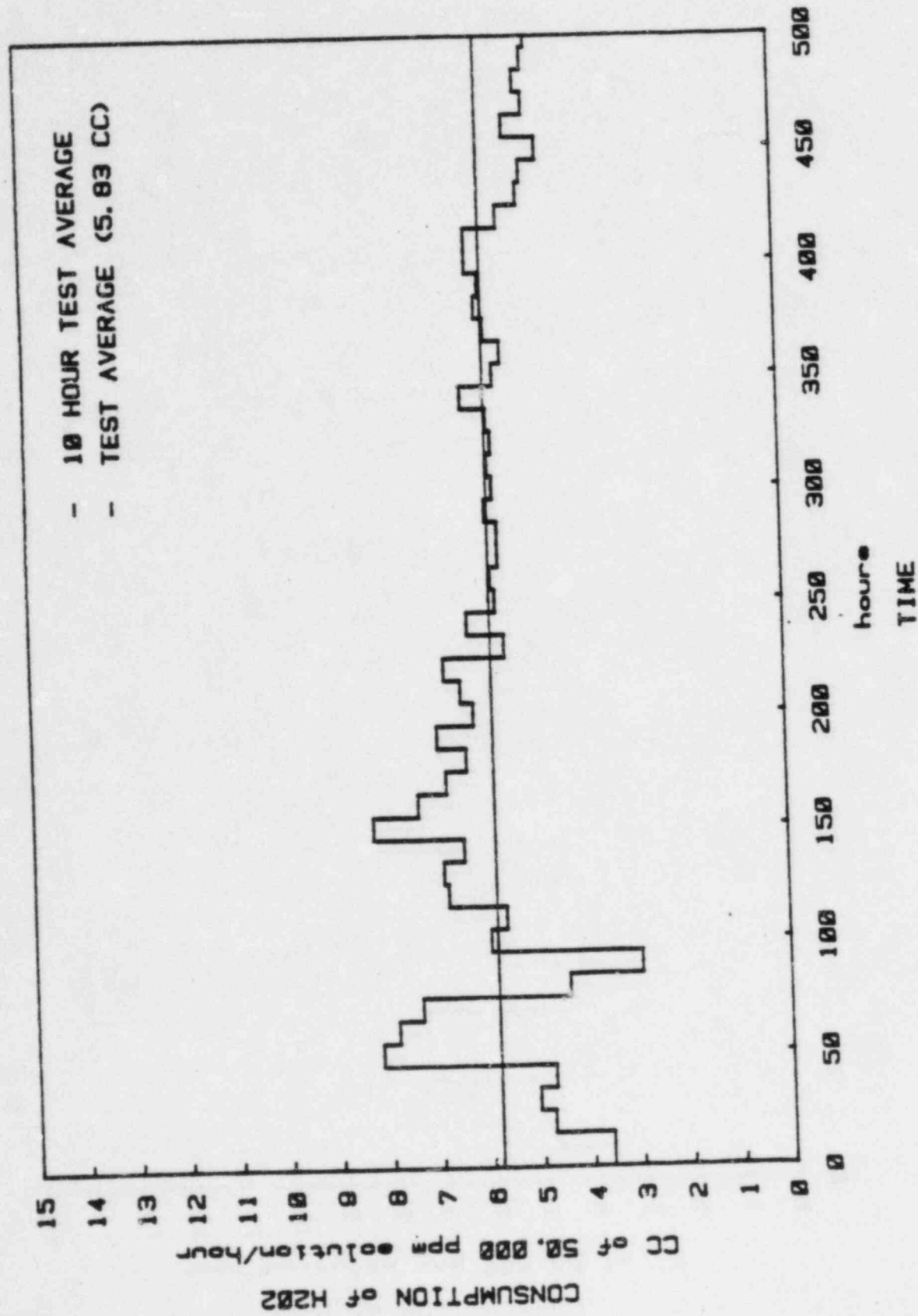


FIGURE 6-5 ESTIMATED H₂O₂ CONSUMPTION RATES

GPU PEROXIDE EXPERIMENT

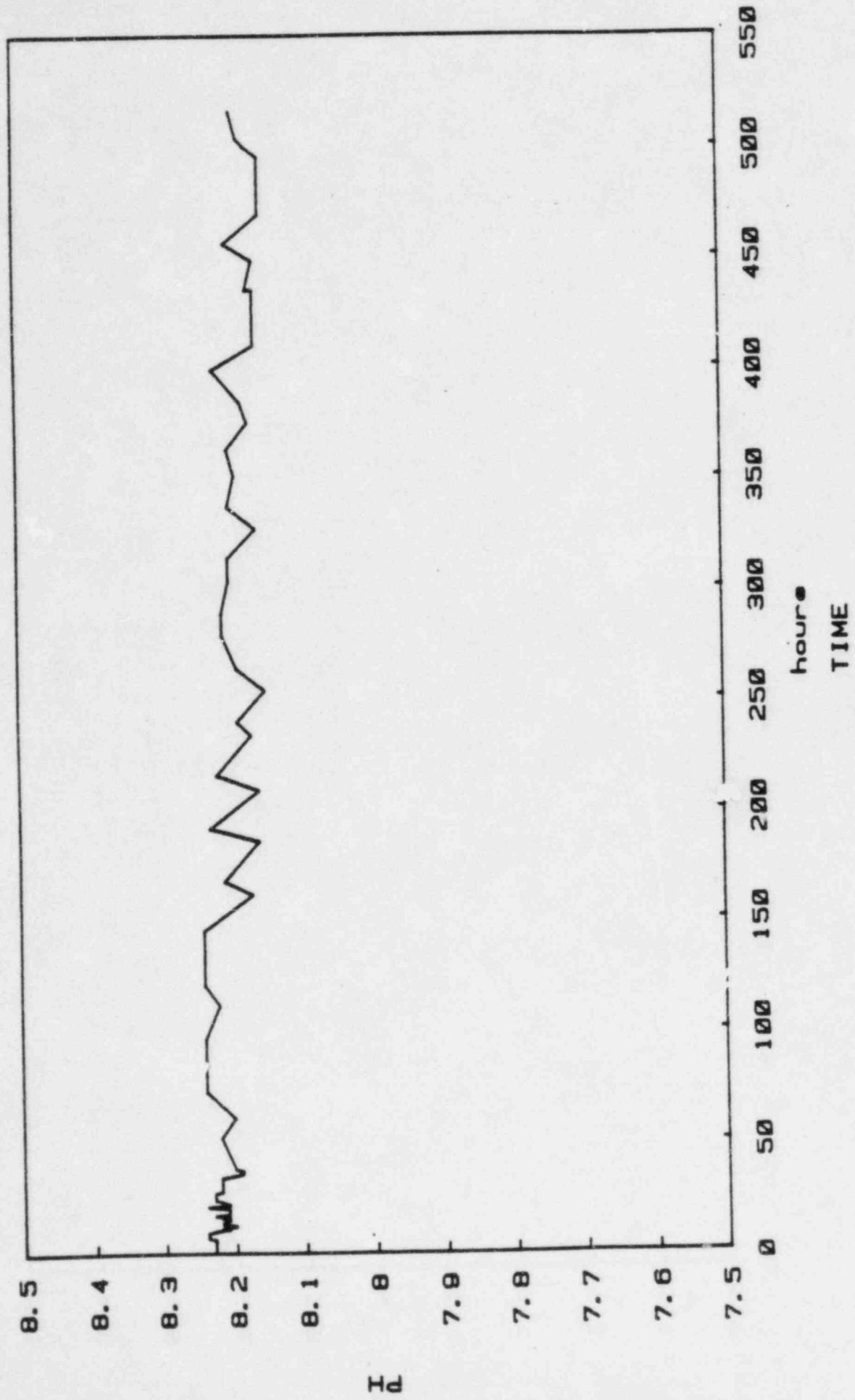


FIGURE 6-6 H₂O₂ EXPERIMENT pH LEVELS

Table 6-1
 AUTOCLAVE SPECIMEN LOADING

<u>Test No.</u>	<u>Full-Size Tube</u>	<u>C-Ring</u>		<u>U-bends</u>		
		<u>Original</u>	<u>Replacement</u>			
1	A13-63	1A1		-		
	(11-18 15/16)	1A2	←2B5 After HFT			
	A24-94	1B1	←1B4 After Cycle 1			
	(19 5/16-25 7/16)	1B2				
		1D1				
		1D2				
		2A1				
		2B1				
		2D1				
		1E1				
		1E2				
		1E3				
	2	B16-21	2A2		←1A5 After HFT	-
		(52-59)	2A4		←2B4 After Cycle 1	
A88-7		2B2				
(2-9 3/4)		2B3				
		2D2				
		2D3				
		1A4				
		1B3				
		1D3				
		1E4				
		1E5				
3	A24-94	-		-		
	(36-42)					
	B94-27					
	(4 1/2-10 1/2)					

Table 6.1 (Continued)

<u>Test No.</u>	<u>Full-Size Tube</u>	<u>C-Ring</u>		<u>U-bends</u>
		<u>Original</u>	<u>Replacement</u>	
4	A16-69 (6 1/2-12 1/4)	P1A1	Removed after H ₂ O ₂ Run	All
		P1A2		
		P1A3		
		P1A4		
		P1A5		
		P2D1	Removed after H ₂ O ₂ Run	
		P2D2		
		P2A1		
		P2A5		
		P1D1		
		P1D2		
		P1D3		
		P1D4		
		P1D5		

TABLE 6-2

ANALYTICAL DATA FOR TEST 1 HFT CYCLE

SOURCE	pH	COND ($\frac{\mu \text{ mho}}{\text{cm}}$)	D.O. (PPM)	Li (PPM)	B (PPM)	F (PPM)	Cl (PPM)	SO ₄ (PPM)	N ₂ H ₄ (PPM)	S ₂ O ₃ (PPM)		
ARGET MUT EMISTRY LEVELS	5.0 to 7.5		<0.010	2.2 to 2.5	2300 to 2400	0.05 to 0.15	0.05 to 0.15	--	2 to 10	0.0585		
TE TAKEN												
/2/82	MUT	6.5	40	<0.005	2.16	2323	0.075	2.22	0.183	0.053	<0.05	NEW MUT
/3/82	EFF				2.21	2332	0.972	58.45	0.908	0.040	<0.05	
/8/82	EFF				2.21	2358	0.06	0.436	0.202	0.086	<0.05	
/10/82	EFF				2.34	2359	0.06	0.282	0.181	0.086	<0.05	
/12/82	MUT	5.6	60	(AIR)	2.28	2352	0.06	0.292	0.178	2.00	<0.05	NEW MUT OPEN TO ATMOSPHERE
/23/82	EFF				1.81	2519	<0.05	0.399	0.168	2.50	<0.05	

SO₄ equivalent = 0.05 to 0.15 PPM.

TABLE 6-3

ANALYTICAL DATA FOR TEST 1 1ST OPERATING CYCLE

SOURCE	pH	COND ($\frac{\mu\text{ mho}}{\text{cm}}$)	D.O. (PIM)	Li (PIM)	B (PIM)	F (PIM)	Cl (PIM)	SO ₄ (PIM)	N ₂ H ₄ (PIM)	S ₂ O ₃ (PIM)	
GET MUT MISTRY LEVELS	5.0 to 7.5		<0.010	2.2 to 2.5	1180 to 1220	0.05 to 0.15	0.05 to 0.15	--	2.0 to 10	0.0585 (AsNa ₂ S ₂ O ₃)	
TE TAKEN											
12/22/82	MUT	6.08	58	<0.002	2.65	1315	<0.05	0.198	0.173	0.698	<0.05
12/28/82	EFF				2.64	1249	<0.05	0.232	0.064	0.041	<0.05
12/29/82	EFF				2.72	1274	<0.05	0.195	0.129	0.046	<0.05
1/04/83	MUT	6.13	50	<0.005	2.56	1217	<0.05	0.161	0.135	0.321	<0.05
1/13/83	EFF				1.83	1260	<0.050	0.236	0.158	8.2	<0.05
1/25/83	EFF				1.96	1258	<0.050	0.223	0.064	4.5	<0.05
1/26/83	MUT	6.13	52	<.005	1.85	1253	<0.050	0.236	0.064	9.8	<0.05 Refill
2/08/83	EFF				2.20	1235	<0.050	0.141	0.028 0.031**	<0.1	
2/11/83	MUT	6.03	53	<.005	2.11	1215	<0.050	0.132	0.050 0.053**	10.6	Refill
2/23/83	EFF				1.95	1203	<0.050	0.137	0.028 0.031**	<0.1	
3/02/83	EFF				2.15	1243 1246			0.088 0.120+		

TABLE 6-4

ANALYTICAL DATA FOR TEST 1 2ND OPERATING CYCLE

SOURCE	pH	COND ($\frac{\mu\text{ mho}}{\text{cm}}$)	D.O. (P/M)	Li (P/M)	B (P/M)	F (P/M)	Cl (P/M)	SO ₄ (P/M)	N ₂ H ₄ (P/M)	S ₂ O ₃ (P/M)	
GET MUT HISTRY LEVELS	5.0			1.7	980	0.05	0.05		2	0.0585	
	to 7.5		<0.010	to 2.0	to 1020	to 0.15	to 0.15	---	to 10	as Na ₂ S ₂ O ₃	
DATE TAKEN											
4/83	MUT	7.10	44.5	<0.005	1.71	1015	< 0.05	0.226	0.131	7.15	<0.05
4/83	EFF				1.60	979	<0.05	⁺ 0.933	0.108+	0.82	<0.05
									0.319		
									0.340		
									0.366#		
9/83	EFF				1.75	1023	<0.05	0.223	0.061	<0.01	<0.05
									0.092+		
21/83	MUT	6.25	--	<0.005	1.70	1028	<0.05	0.227	0.114	8.30	<0.05
23/83	EFF				1.81	1040	<0.01	0.302	0.038	<0.01	<0.05
16/83	EFF				1.52	1042	<0.01	0.296	0.033	0.02	<0.05
18/83	MUT	6.07	38	<0.005	1.71	1046	<0.01	0.274	0.056	16.5	<0.05
23/83	EFF				1.62	1030	<0.01	0.287	0.028	0.02	<0.05

Duplicate Analysis
Recheck 6/17/83
GPU Designation

TABLE 6-5

ANALYTICAL DATA FOR TEST 2 HFT CYCLE

SOURCE	pH	COND ($\frac{\mu\text{ mho}}{\text{cm}}$)	D.O. (PIM)	Li (PIM)	B (PIM)	F (PIM)	Cl (PIM)	SO ₄ (PIM)	N ₂ H ₄ (PIM)	S ₂ O ₃ (PIM)	
GET MUT MISTRY LEVELS	5.0 to 7.5		<0.010	2.2 to 2.5	2300 to 2400	0.05 to 0.15	0.05 to 0.15	0.05 to 0.15	2 to 10	--	
E TAKEN											
/19/82	MUT	5.73	42	<0.005	2.2	2395	0.02	0.06	0.115	"evidence"	Research Analysis
/22/82	MUT				1.90	2341	0.08	0.08	0.08	2.75	Waltz Mill Analysis
		-----SPIKED MUT WITH F ⁻ , Cl ⁻ -----									
/25/82	MUT				1.97	2296	0.06	0.118	0.388	5.27	
/25/82	EFF				2.10	2303	2.38	1.23	0.511	0.15	--
/28/82	MUT				2.01	2315	0.041	0.102	0.214	0.44	<0.05
/28/82	EFF				1.98	2305	0.47	0.47	0.24	0.018	
/2/82	MUT	5.6	38	(Air)	2.00	2297	0.073	0.100	0.234	0.76	<0.05 MUT Refill Open to Air
/11/82	MUT				2.07	2350	0.06	0.155	0.220	0.193	<0.05
/11/82	EFF				2.07	2348	0.05	0.248	0.236	0.079	<0.05

TABLE 6-6
ANALYTICAL DATA FOR TEST 2 1ST CYCLE

SOURCE	pH	COND ($\frac{\mu\text{ mho}}{\text{cm}}$)	D.O. (PIM)	Li (PIM)	B (PIM)	F (PIM)	Cl. (PIM)	SO ₄ (PIM)	N ₂ H ₄ (PIM)	S ₂ O ₃ (PIM)	
GET MUT MISTRY LEVELS	5.0 to 7.5		<0.010	2.2 to 2.5	1180 to 1220	0.05 to 0.15	0.05 to 0.15	0.05 to 0.15	2 to 10	---	
E TAKEN											
3/82	MUT			2.07	1310	<0.05	0.323	0.171	0.02		
10/82	MUT	6.5	40	<0.005	1.94	1119	<0.05	0.296	0.140	3.24	REFILL MUT 12/8/82
10/82	EFF			1.95	1281	<0.05	1.60	0.245	0.05		
10/82	EFF			1.88	1185	<0.05	0.538	0.200	<0.01		
12/21/82	MUT	6.03	52	<0.005	2.16	1205	<0.05	0.146	0.039 0.136+	0.005	REFILL MUT
12/23/82	EFF			2.25	1196	<0.05	0.148	0.037 0.150+	0.005		
1/5/83	EFF			2.14	1209	<0.05	0.163	0.033	0.012		
11/1/83	MUT	6.00	67	<0.005	1.87	1205	<0.05	0.217	0.098	4.6	<0.05 REFILL
11/26/83	EFF			1.93	1187	<0.05	0.236	0.097	<1	<0.05	
12/1/83	MUT	6.10	51	<0.005	2.15	1214	<0.050	0.138	0.160 0.179	8.0	REFILL
12/8/83	EFF			1.95	1204	<0.050	0.147	0.145 0.152	<0.1		
12/16/83	EFF			2.30	1203	<0.050	0.151	0.206 0.221	0.11		
12/17/83	EFF			2.29	1203	<0.050	0.127	0.179 0.197	3.6		

*Concentrator Column.

TABLE 6-7

ANALYTICAL DATA FOR TEST 2 2ND OPERATING CYCLE

SOURCE	pH	COND ($\frac{\mu\text{mho}}{\text{cm}}$)	D.O. (PPM)	Li (PPM)	B (PPM)	F (PPM)	Cl (PPM)	SO ₄ (PPM)	N ₂ H ₄ (PPM)	S ₂ O ₃ (PPM)	
	5.0 to 7.5		<0.010	1.7 to 2.0	980 to 1020	0.05 to 0.15	0.05 to 0.15	0.05 to 0.15	0.05 to 0.15	---	
MUT	6.50	70	<0.005	1.48	998	<0.05	0.242	0.171	0.40		New
EFF				1.47	990	<0.05	0.236	0.283	0.28		
MUT	6.17	33	<0.005	1.76	1026	<0.05	0.236	{ 0.135 0.142 0.175## }	0.22		Refill
EFF				1.70	1019	<0.05	0.227	{ 0.164 0.166## }	0.02		
EFF				1.72	1060	<0.010	0.279	0.130	<0.01		
EFF				1.79	1024	<0.010	0.286	0.121	<0.01		
MUT	6.24	--	<0.005	1.72	1037	<0.010	0.276	0.119	12.41		
EFF				1.74	1037	<0.010	0.282	0.111	0.02		

Ion Chromatography Loop

Table 6-8
ANALYTICAL CHEMISTRY RESULTS FOR LOOP 3
DURING CLEANUP AND PRECONDITIONING

<u>Date</u>	<u>Sample Source</u>	<u>SO₄² (PPM)</u>	<u>B (PPM)</u>	<u>Li (PPM)</u>	<u>Remarks</u>
2/3/83	EFF	2.950	--	--	Final Water Flush
2/4/83	MUT	0.148	--	--	Preconditioning
2/4/83	EFF	1.200	--	--	Preconditioning
2/7/83	MUT	0.150	--	--	Preconditioning
2/7/83	EFF	0.154	--	--	Preconditioning
2/8/83	MUT	0.150	--	--	Preconditioning
2/8/83	EFF	0.152	--	--	Preconditioning
2/9/83*	MUT	0.142	2389	2.04	Preconditioning
2/9/83*	EFF	0.154	2296	1.92	Preconditioning

*Analysis performed at Waltz Mill; others done at Westinghouse Research and Development Center

Table 6-9
ANALYTICAL CHEMISTRY RESULTS FOR LOOP 4 DURING
CLEANUP AND PRECONDITIONING

<u>Date</u>	<u>Sample Source</u>	<u>SO₄² (PPM)</u>	<u>B (PPM)</u>	<u>Li (PPM)</u>	<u>Remarks</u>
2/8/83	MUT	0.007	--	--	H ₂ O Flush
2/9/83	EFF	0.225	--	--	Final Flush Sample
2/10/83	MUT	0.147	--	--	Preconditioning
2/10/83	EFF	0.810	--	--	Preconditioning
2/11/83	MUT	0.152	--	--	Preconditioning
2/11/83	EFF	0.373	--	--	Preconditioning
2/14/83	MUT	0.155	--	--	Preconditioning
2/14/83	EFF	0.183	--	--	Preconditioning
2/15/83	MUT	0.150	--	--	Preconditioning
2/15/83	EFF	0.340	--	--	Preconditioning
2/16/83	MUT	0.150	--	--	Preconditioning
2/16/83	EFF	0.175	--	--	Preconditioning
*2/17/83	MUT	0.135	2385	2.11	Preconditioning
*2/17/83	EFF	0.147	2294	2.57	Preconditioning

*Analysis performed at Waltz Mill; others done at Westinghouse R+D.

Table 6-10

APPARATUS CHANGES AND EVENTS: PEROXIDE CLEANING RUNS

<u>Date</u>	<u>Event</u>	<u>Action</u>	<u>Result</u>
2/22/83	No mixing of chemical additions in MUT	Attached peristaltic pump to MUT to function as a mixing loop	Better solution homogeneity
2/24/83	Hourly H ₂ O ₂ addition	Added automatic H ₂ O ₂ injector to system	Steady addition of peroxide to the system (5 ml/h initially)
2/25/83	Plastic line on peristaltic pump broke	Replaced line	8 L of solution lost before repair
2/25/83	Rupture disk broke. Solution pumped to drain.	Replaced disk, replumbed so that in event of a future rupture the solution would be returned to the MUT	19 L of solution lost before repair
2/26/83	Line on peristaltic pump failed again	Replaced line and peristaltic pump with a centrifugal rotary pump	8 L of solution lost before repair
2/26/83	Low MUT Level	Added 50 L of solution	54.85 L in MUT
2/28/83	Low flow (1.8 gph) through samples	Checked and replaced rupture disk	No disk rupture; possible leakage
3/16/83	AC pressure gauge broken on autoclave 4	None	Possibility there was a bulk AC pressure throughout the entire test period

Table 6-11
 AVERAGE DAILY MAKE-UP TANK PEROXIDE
 CONCENTRATIONS AND pH VALUES

<u>Date</u>	<u>Average H₂O₂ Concentration (ppm)</u>	<u>Average pH</u>
2/22/83	15.0 ± 0 (5)*	8.233 ± 0.004 (3)*
2/23/83	14.9 ± 2.3 (28)	8.219 ± 0.008 (24)
2/24/83	17.8 ± 3.4 (28)	8.211 ± 0.012 (9)
2/25/83	17.9 ± 3.3 (24)	8.243 (1)
2/26/83	15.6 ± 2.2 (24)	8.240 ± 0.0 (2)
2/27/83	16.5 ± 1.2 (22)	8.230 ± 0.010 (2)
2/28/83	17.2 ± 1.9 (24)	8.195 ± 0.045 (2)
3/01/83	17.8 ± 1.4 (24)	8.190 ± 0.020 (2)
3/02/83	18.2 ± 1.4 (24)	8.195 ± 0.035 (2)
3/03/83	18.5 ± 1.6 (24)	8.190 ± 0.030 (2)
3/04/83	18.7 ± 0.7 (24)	8.180 ± 0.010 (2)
3/05/83	18.4 ± 0.7 (24)	8.170 ± 0.020 (2)
3/06/83	18.5 ± 0.8 (24)	8.210 ± 0.000 (2)
3/07/83	17.6 ± 0.6 (24)	8.200 ± 0.000 (2)
3/08/83	17.5 ± 1.4 (24)	8.180 ± 0.020 (2)
3/09/83	18.3 ± 1.1 (24)	8.195 ± 0.005 (2)
3/10/83	17.4 ± 1.1 (24)	8.175 ± 0.005 (2)
3/11/83	17.6 ± 1.4 (24)	8.190 ± 0.030 (2)
3/12/83	19.4 ± 1.0 (24)	8.16 (1)

(continued)

Table 6-11 (Continued)

<u>Date</u>	<u>Average H₂O₂ Concentration (ppm)</u>	<u>Average pH</u>
3/13/83	18.4 ± 1.3 (24)	8.180 ± 0.020 (2)
3/14/83	18.7 ± 0.9 (24)	8.150 ± 0.000 (2)
3/15/83 (up to shutdown initiation)	18.3 ± 0.9 (17)	8.160 ± 0.010 (2)

* The number in () is the number of readings over which the average is taken. The peroxide concentrations were generally determined hourly (approximately), and the pH was usually read twice daily.

Table 6-12
DAILY PEROXIDE USAGE
(50,000 ppm H₂O₂ Solution)

<u>Date</u>	<u>Total Hours</u>	<u>ml Used</u>	<u>Total Weight H₂O₂/Day (g)</u>	<u>Average weight H₂O₂ per Hour (mg/h)</u>
2/22/83	3.55	27.2	1.360	383
2/23/83	24	135	6.750	281
2/24/83	24	198.3	9.915	413
2/25/83	24	120	6.000	250
2/26/83	24	192	9.600	400
2/27/83	24	192	9.600	400
2/28/83	24	192	9.600	400
3/01/83	24	202	10.100	421
3/02/83	24	192	9.600	400
3/03/83	24	191	9.550	398
3/04/83	24	192	9.600	400
3/05/83	24	192	9.600	400
3/06/83	24	192	9.600	400
3/07/83	24	192	9.600	400
3/08/83	24	178	8.900	371
3/09/83	24	165	8.250	344
3/10/83	24	175	8.750	365
3/11/83	24	179	8.950	373
3/12/83	24	154	7.700	321
3/13/83	24	154	7.700	321
3/14/83	24	143	7.150	298
3/15/83	16	101	5.050	316

may be lower than reported

TABLE 6-13

PEROXIDE LOOP ANALYTICAL DATA

<u>DATE</u>	<u>TIME 24 HOUR CLOCK</u>	<u>SAMPLE SOURCE</u>	<u>CUMULATIVE RUNNING HOURS</u>	<u>SO₄² (PPM)</u>	<u>B (PPM)</u>	<u>LI (PPM)</u>	<u>REMARKS</u>
2/18/83		MJT		0.052	2534	2.05	No Recirculation
2/18/83	1406	EFF		0.273	2573	2.14	System Flush
2/22/83	1850	AC EFF		0.400	2581	2.29	From AC Bleed Line
2/22/83	1900	EFF		0.863	2579	2.44	Initial Sol'n. Through Specimens
2/22/83	2010	---	Start 00:00	---	--	--	
2/23/83	0932	EFF	13:22	0.284	2579	2.53	
2/23/83	1230	EFF	16:20	0.305	2590	2.58	
2/24/83	0930	EFF	37:22	0.344	2584	2.54	
2/25/83	1130	EFF	63:20	0.388	2648	1.67	
2/25/83	2100	EFF	71:50	0.388	2542	1.59	
2/26/83	1110	MJT	87:00	0.209	2407	1.59	
2/27/83	2100	EFF	120:50	0.243	2423	1.54	
2/28/83	1045	EFF	134:35	0.226	2420	1.56	
2/28/83	2200	EFF	145:50	0.263	2392	1.85	
03/01/83	1100	EFF	158:50	0.263	2373	1.88	
03/01/83	2000	EFF	167:50	0.305	2386	1.86	
03/02/83	1110	EFF	183:00	0.243	2387	1.54	
03/02/83	2000	EFF	191:50	0.300	2375	1.89	
03/03/83	1330	EFF	209:30	0.305	2390	1.86	
03/03/83	2000	EFF	215:50	0.320	2368	1.87	
03/04/83	1340	EFF	233:30	0.308	2351	1.94	
03/04/83	2000	EFF	239:50	0.313	2375	1.87	

TABLE: 6-13 (CONT'D)
PEROXIDE LOOP ANALYTICAL DATA

<u>DATE</u>	<u>TIME 24 HOUR CLOCK</u>	<u>SAMPLE SOURCE</u>	<u>CUMULATIVE RUNNING HOURS</u>	<u>SO₄² (PPM)</u>	<u>B (PPM)</u>	<u>Li (PPM)</u>
3/5/83	1005	EFF	253:50	0.316	2370	1.88
3/5/83	2000	EFF	263:50	0.305	2351	1.85
3/6/83	1100	EFF	278:50	0.311	2370	1.97
3/6/83	2100	EFF	288:50	0.313	2362	1.82
3/7/83	1105	EFF	303:00	0.315	2364	1.91
3/7/83	2200	EFF	313:50	0.306	2311	1.81
3/8/83	2100	EFF	336:50	0.290	2313	1.79
3/9/83	1115	EFF	351:05	0.293	2331	1.79
3/9/83	2300	EFF	361:50	0.322	2331	1.78
3/10/83	1130	EFF	375:20	0.286	2335	1.74
3/10/83	2000	EFF	383:50	0.318	2302	1.80
3/11/83	1115	EFF	399:05	0.354	2322	1.76
3/11/83	2200	EFF	409:50	0.340	2318	1.82
3/12/83	1100	EFF	422:50	0.325	2285	1.78
3/12/83	2300	EFF	434:50	0.345	2289	1.79
3/13/83	1115	EFF	447:05	0.325	2287	1.86
3/13/83	2300	EFF	458:50	0.332	2296	1.86
3/14/83	1105	EFF	470:55	0.309	2280	1.77
3/14/83	2300	EFF	482:50	0.317	2269	1.79

TABLE 6-13 (CONT'D)
PEROXIDE LOOP ANALYTICAL DATA

<u>DATE</u>	<u>TIME 24 HOUR CLOCK</u>	<u>SAMPLE SOURCE</u>	<u>CUMULATIVE RUNNING HOURS</u>	<u>SO₄² (PPM)</u>	<u>B (PPM)</u>	<u>Li (PPM)</u>
3/15/83	1115	EFF	495:05	0.324	2285	1.84
3/15/83	1600	EFF	499:50	0.331	2285	1.80
3/15/83	1930	MUT	503:20	0.327	2287	1.79
3/16/83	0800	MUT	515:50	0.365	2289	1.71
3/16/83	0800	EFF	515:50	0.370	2267	1.68
3/16/83	1930	EFF	527:20	0.348	2236	1.72

EFF = Loop Effluent
MUT = Make-Up Tank

7.0 RESULTS

At the end of each cycle, the specimens were removed and the C-rings were stereomicroscopically examined. Full size tubes were then eddy current examined while one C-ring was removed for weighing and metallographic examination. Occasionally additional examination techniques such as SEM or ESCA were employed.

7.1 Visual Examination

The results of the C-ring stereomicroscopic examinations to date are summarized in Tables 7-1, 7-2 and 7-3. The examinations are subjective in nature and have been reduced to a tabular form for presentation.

Interpretation is difficult since most of the tubes had significant surface abnormalities in the as-received condition. The primary observation following the peroxide exposure was that the material in the ID pits, which pits are typical of the ID surfaces of the as-received OTSG tubing samples, exhibited a discoloration with respect to adjacent ID surface films. This usually darker discoloration differentiated the pits from the adjacent surface regions to an extent that the pits appeared anomalous and possibly active. However, the number of pits, the randomness of distribution of the pits, and the sizes of the pits were typical of other C-ring samples which were not exposed to the peroxide clean-up chemistry. Since later examinations of these peroxide pre-exposed samples following subsequent exposure to normal reactor coolant chemistry and temperatures gave observations which were typical of all other samples, the anomalous appearance of the material in the pits following the peroxide run is potentially interpretable in terms of differences in the reactivity or response of the deposits as governed by solution accessibility and/or localized variations in the deposit topology.

Since destructive examination of U-bend specimens was not performed after the peroxide run, the effect of the peroxide exposure on these materials was based on visual examination of the specimen surfaces. These examinations showed no surface abnormalities. The peroxide exposure therefore, had no visually detrimental effects on these materials. Following completion of the testing, destructive examination of these specimens will permit a more detailed

evaluation of the combined effects of the peroxide, HFT, and operational cycles.

Most of the specimens that had been through the long term corrosion test cycles have significant mechanical markings (scratches and score marks) and pitting. However, these were generally associated with the "as received" surface features.

Figures 7-1 through 7-6 show before and after photomicrographs of the specimens removed from the experiments for metallographic analysis. The view is looking through the C-ring cutout slot at the stressed ID surface.

7.2 Weight Changes

Weight changes of C-rings removed from test to date are shown in Table 7-4. The average change was a 0.02 percent weight loss.

7.3 Metallographic Examination

A metallographic examination was made of each C-ring removed from the test. Each specimen was transversely sectioned. One midplane and one end surface were mounted and polished. Etched surfaces were prepared by a 60 second exposure to concentrated HCl, methanol rinse, 5-10 second exposure to 2 percent bromine in methanol, and two additional methanol rinses.

Typical micrographs of the stressed region, ID surfaces of each specimen are shown in Figures 7-7 through 7-12. No unusual surface features were observed in any of the specimens. Surfaces examined to date have shown intergranular attack to a maximum depth of one to two grains.

7.4 Auger and X-ray Photoelectron Spectroscopy (XPS) Analyses for Sulfur Pickup by New Surfaces of OTSG Tubing

Appendix 10.6 describes the experimental methodology for preparation of ion-implanted sulfur standards and the microanalytical procedures.

Archive OTSG tubing samples, which had not been service-exposed in the TMI-1 plant, were exposed to a pre-conditioning in loop 3 at elevated temperature in simulated reactor coolant. Auger and XPS studies of these conditioned samples and the standards gave the following three results.

1. The analysis of ion implanted standards showed that Auger electron spectroscopy can detect quantities of sulfur as low as $3 \times 10^{-9} \text{ g/cm}^2$ ($3 \mu\text{g/ft}^2$) if distributed within the first 10 nm below the surface. If such an amount of sulfur were distributed uniformly through a 100 nm thick region below the surface, the total detectable sulfur content would be $0.03 \mu\text{g/cm}^2$ ($30 \mu\text{g/ft}^2$). Amounts lower than that could escape detection.
2. The conditioned samples showed significant boron contamination, absent in the standards. The Auger signal for the boron compound (unidentified) consisted of a major peak at 170 eV and a minor peak at 152 eV. The latter may interfere with the sulfur peak at 148 eV and increase the sulfur levels that can go undetected by a factor of ten or more. No peak overlap occurred in XPS, however, and the XPS detection limit for sulfur was determined to be five times that of AES, or $0.15 \mu\text{g/cm}^2$ ($150 \mu\text{g/ft}^2$) within the first 100 nm.
3. No sulfur was detected in any of six areas analyzed on conditioned specimens. It is concluded that those specimens contained less than $0.15 \mu\text{g/cm}^2$ ($150 \mu\text{g/ft}^2$) of sulfur within the first 100 nm below the surface and less than $0.015 \mu\text{g/cm}^2$ ($15 \mu\text{g/ft}^2$) within the first 10 nm.

7.5 Eddy Current Inspection Results

In September, 1982, the Field Data Analysis section of Westinghouse Nuclear Energy Systems undertook eddy current testing of a number of long term corrosion test tube samples which had been removed from the Three Mile Island (TMI) Unit No. 1 steam generators. A baseline multiple frequency eddy current inspection was performed at test frequencies which were specified by GPU-N. A list of eighteen tubes which were inspected is contained in Table 7-5. All eighteen tubes were eddy current inspected using a differential bobbin probe and test frequencies of 45 KHz, 200 KHz, 400 KHz, and 800 KHz.

The calibration standard consisted of a section of archive tubing with a 0.052 inch diameter thru-wall drilled hole. The phase angle of the drilled hole was set at 40° for all frequencies. The 400 KHz drilled hole signal is shown in Figure 7-13. A section of OTSG tubing with machined partial ID indications, which was to be used for 'repair' tests, was not employed in this phase of the program.

Indications were noted on five tubes during the baseline inspection:

<u>Tube</u>	<u>Section</u>	<u>Indication</u>
A16-69 (Fig. 7-14)	2"-6-1/2"	95 percent I.D.
A13-63 (Fig. 7-15)	20-9/16"-23-9/16"	Small dent
A88-7 (Fig. 7-16)	2"-9-3/4"	82 percent I.D.
A13-63 (Fig. 7-17)	11"-20-9/16"	< 20 percent O.D.
A24-94	19-5/16"-25-7/16"	96 percent I.D. 30 percent O.D.

Additional eddy current testing was performed upon completion of each cycle of operation of each autoclave loop. A summary of these inspections is presented in Table 7-5 with further explanation following.

On November 15, 1982, tubes B16-22 and A88-7 were reinspected after their first cycle of autoclave testing (the "HFT" cycle). There appeared to be no change in the signal from the indication on A88-7 (Figure 7-18) and no indications were noted on B16-22.

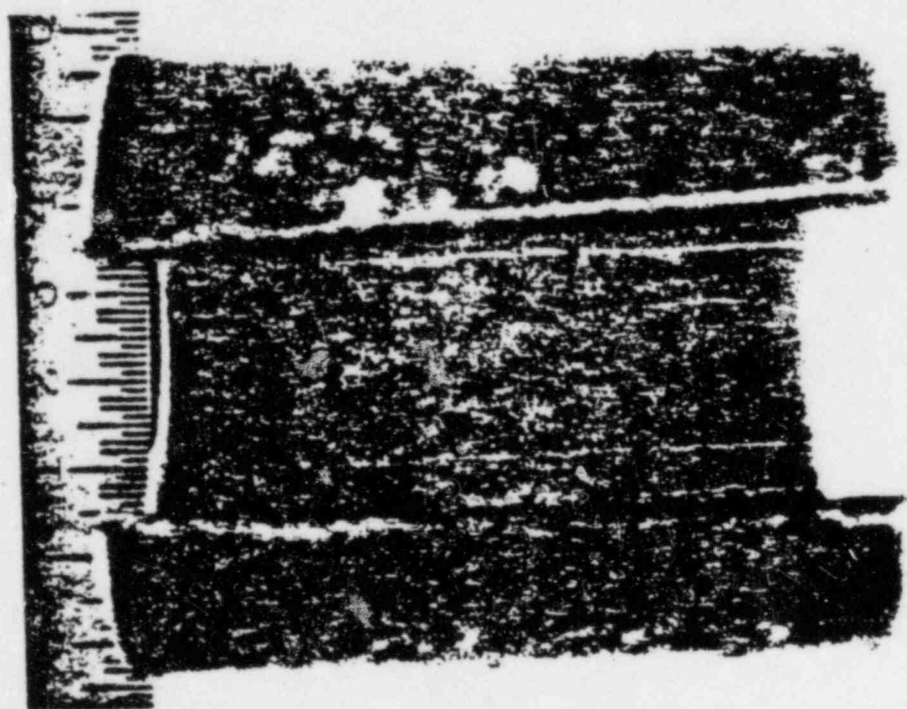
Tubes A24-94 and A13-63 were reinspected on November 30, 1982, following their first ("HFT") autoclave cycle. Tube A13-63 (Figure 7-19) exhibited a thru wall indication. Tube A24-94 (Figure 7-20) exhibited the previously observed 30 percent O.D. indication.

Three tubes were inspected on February 15, 1983. Tubes A24-94, 36" to 42", and B94-27, 4-1/2" to 10-1/2" showed no indications. Tube A16-69, 6-1/2" to 12-1/4" exhibited an I.D. indication the size of which was difficult to estimate due to a distortion of the signal (Figure 7-21). It is estimated that this indication could be as much as 80 percent thru wall. Subsequent inspections of this tube showed this indication consistently in the range of 60 to 80 percent.

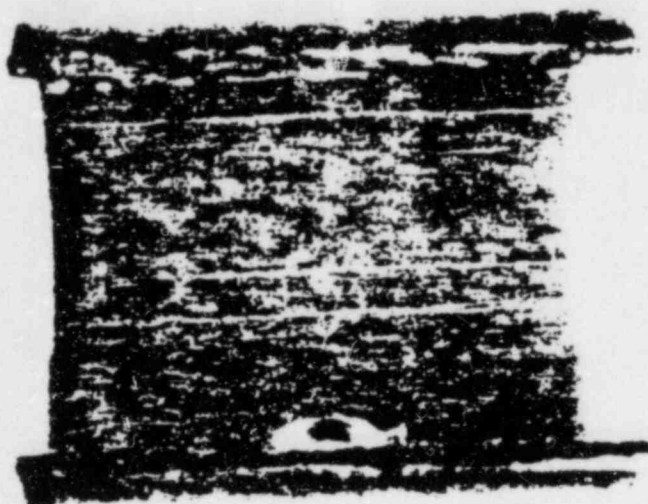
Inspections of tubes A88-7 and B16-22, 52"-59", were performed on February 22, 1983. As can be seen from Figure 7-22, there was no change in the signal for tube A88-7. No indications were observed in tube B16-22.

Tubes A13-63 and A24-94 were reinspected on March 2, 1983. There was essentially no change in the indications previously observed on these tubes. A copy of the signal for tube A13-63 is provided in Figure 7-23.

On March 23, 1983, Tubes A16-69, B94-27, and A24-94, 36" to 42" were reinspected. The indication on A16-69 (Figure 7-24) remained the same and no indications were observed on B94-27 and A24-94.

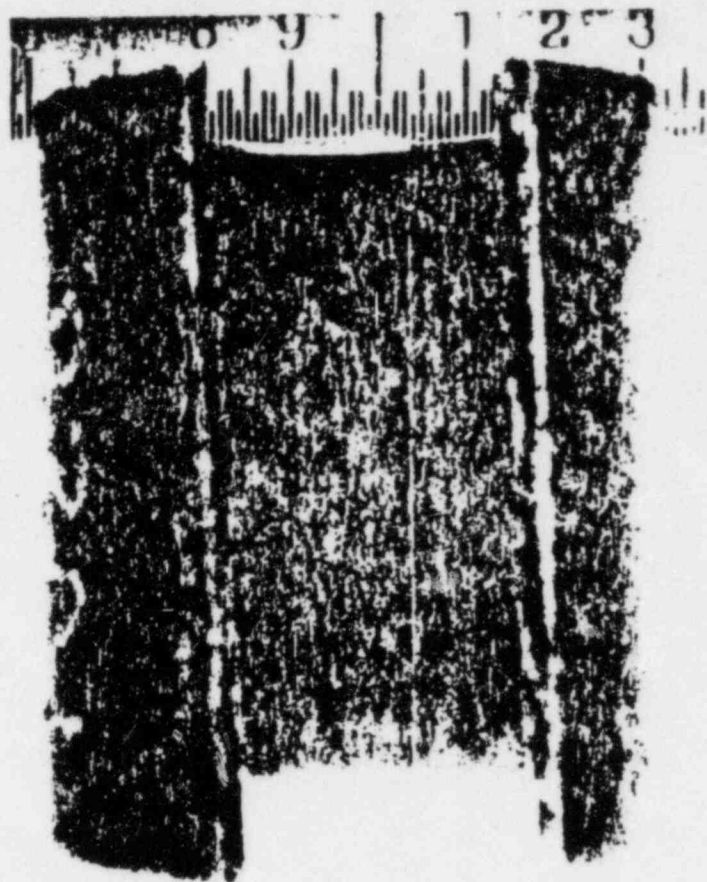


AS RECEIVED



AFTER H₂O₂ EXPERIMENT

Figure 7.1. Macrographs of Specimen P1A1

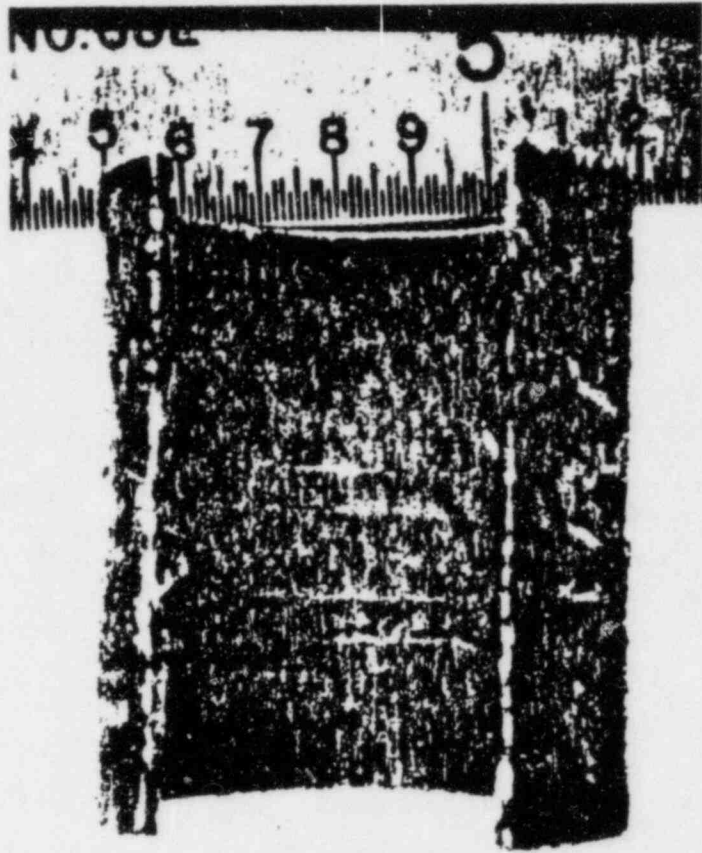


AS RECEIVED



AFTER H₂O₂ EXPERIMENT

Figure 7.2. Macro photograph of Specimen P2A1



AS RECEIVED



AFTER HFT

Figure 7.3. Macro photograph of Specimen 1A2

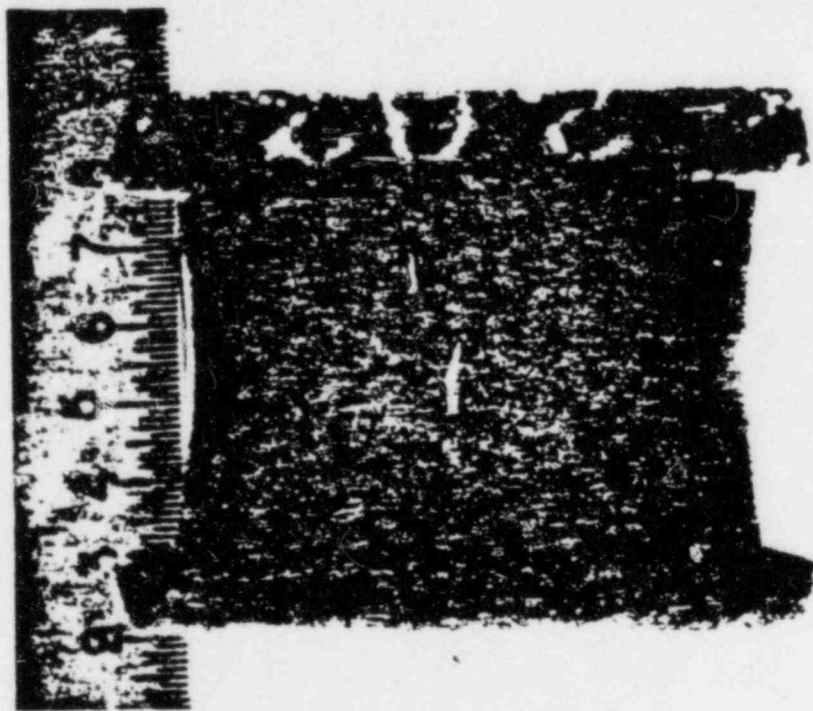


AS RECEIVED

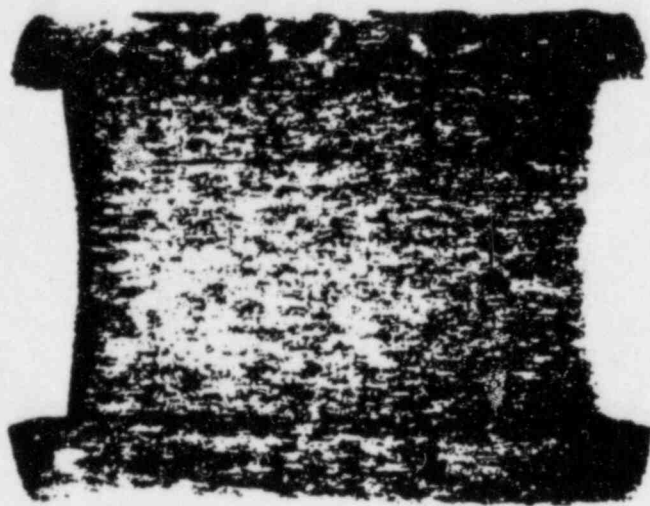


AFTER 1ST OPERATION CYCLE

Figure 7.4. Macro photograph of Specimen 1B1

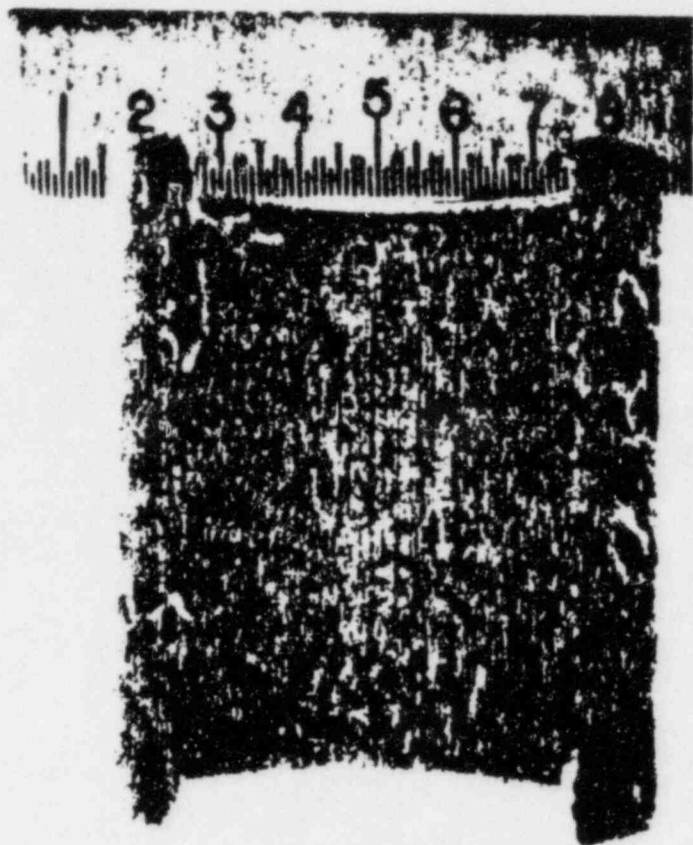


AS RECEIVED



AFTER HFT

Figure 7.5. Macro photograph of Specimen 2A2



AS RECEIVED



AFTER 1ST OPERATION CYCLE 4

Figure 7.6. Macro photograph of Specimen 2B2

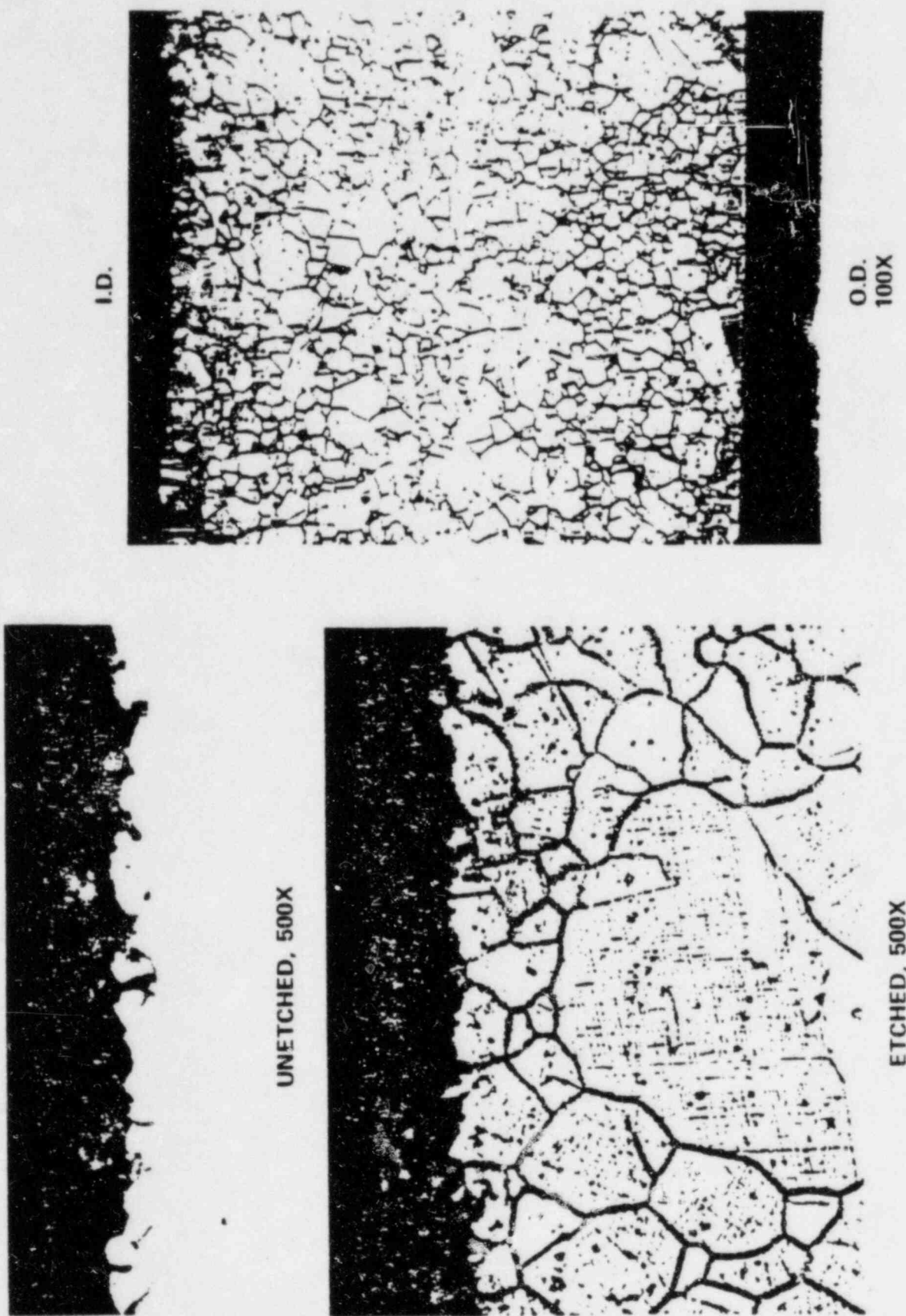
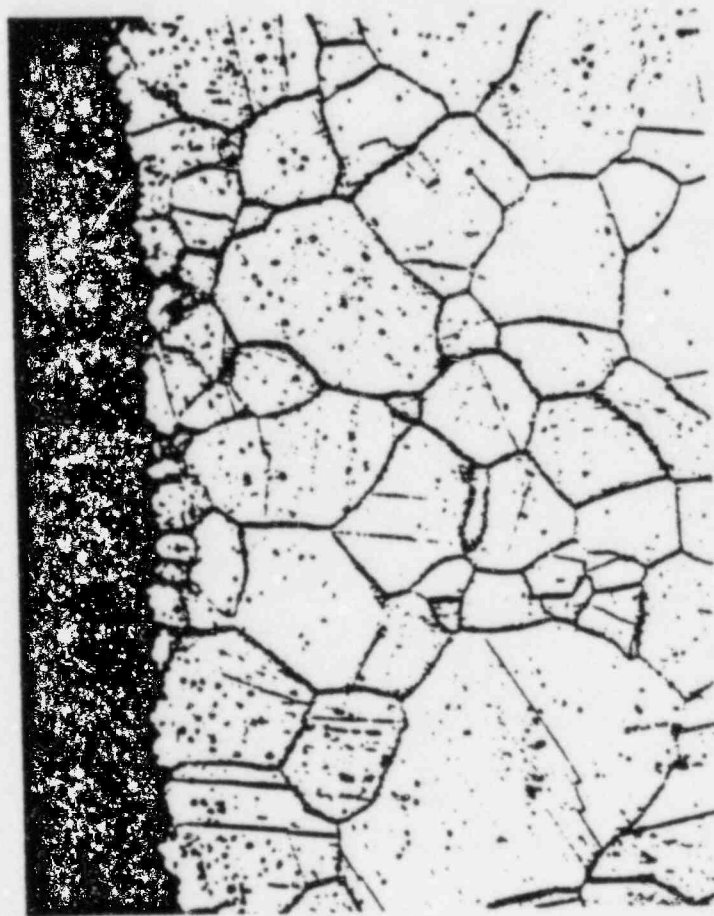


Figure 7.7. Micrographs of Specimen P1A1 I.D. Stressed Regions After H₂O₂ Experiment

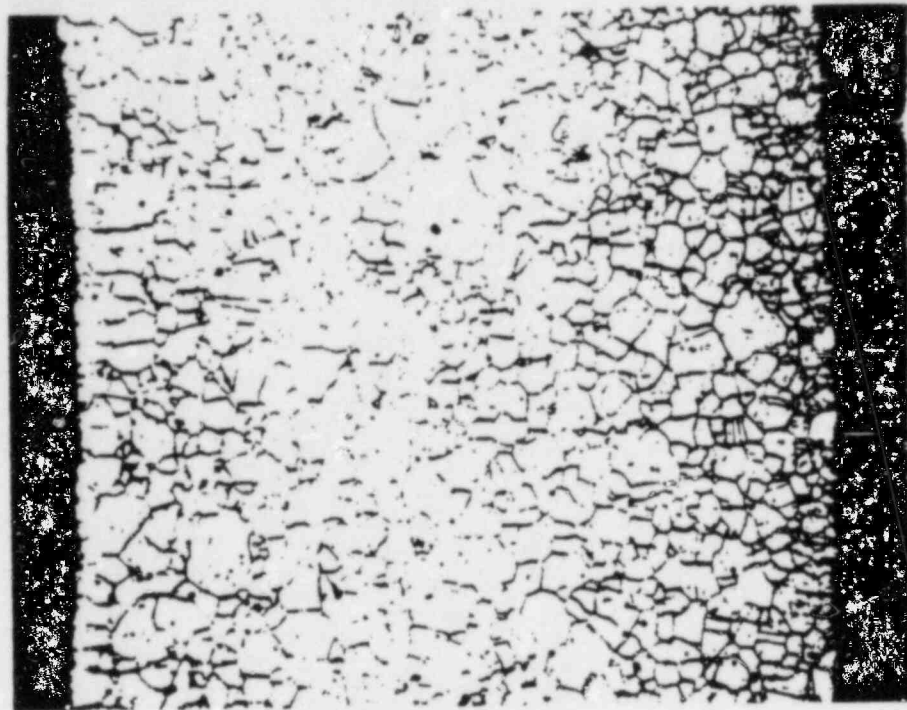


UNETCHED, 500X



ETCHED, 500X

I.D.

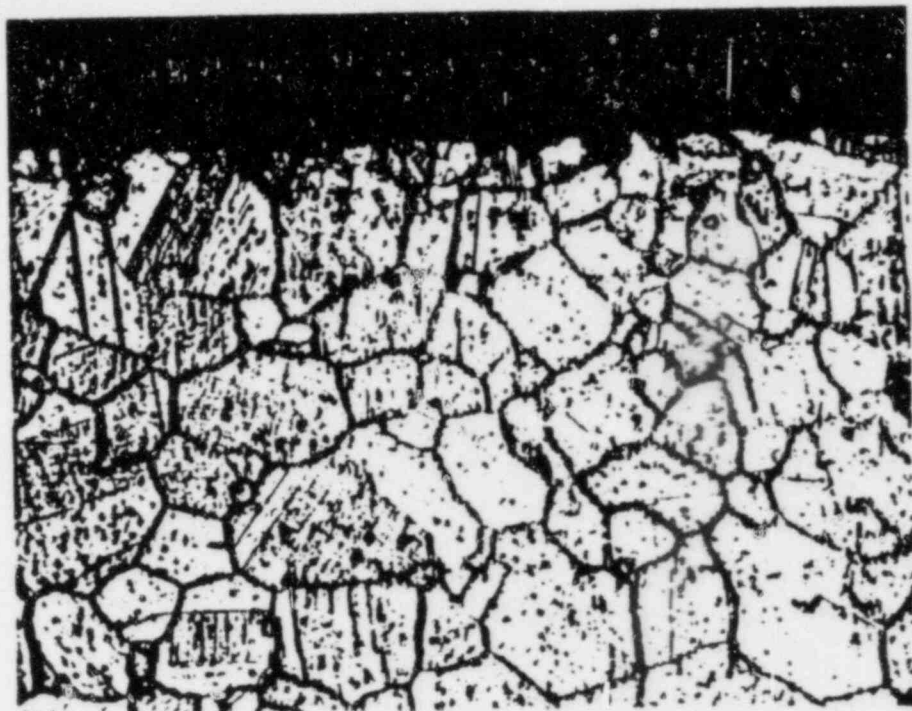


O.D.
100X

Figure 7.8. Micrographs of Specimen P2A1 I.D. Stressed Region After H₂O₂ Experiment

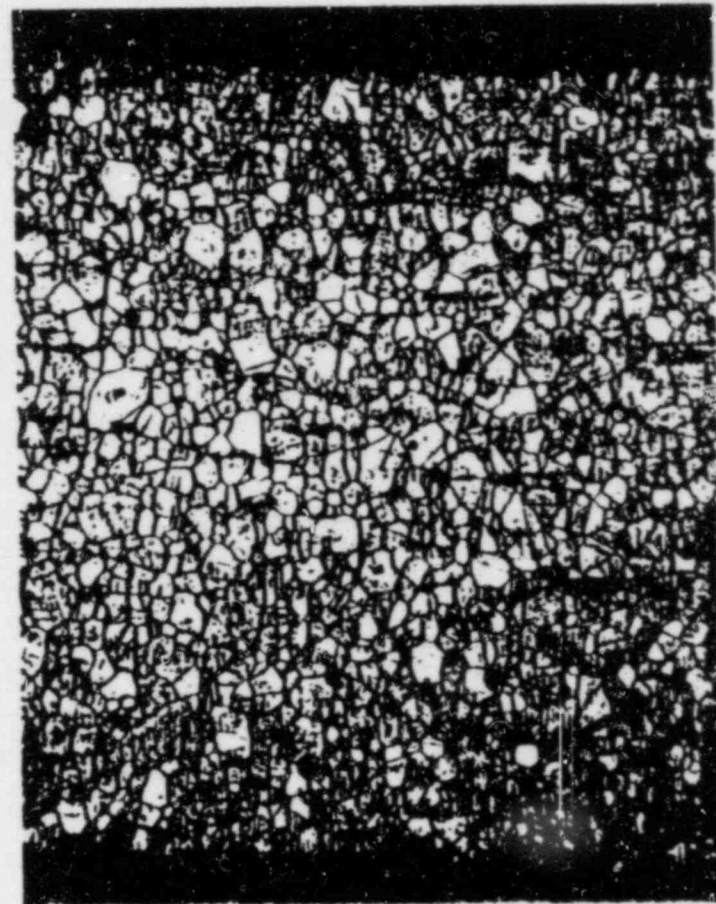


UNETCHED, 500X



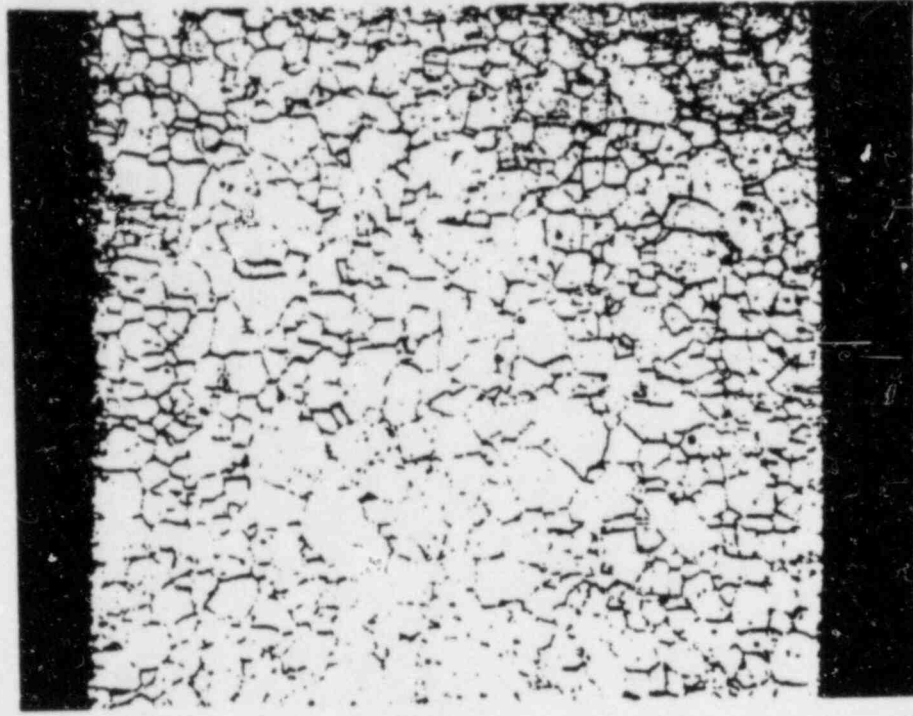
ETCHED, 500X

I.D.



O.D.
100X

Figure 7.9. Micrograph of Specimen 1A2, I.D. Stressed Region After HFT



I.D.

O.D.

100X



500X

Figure 7.10. Micrograph of Specimen 1B1, I.D. Stressed Region After 1st Cycle

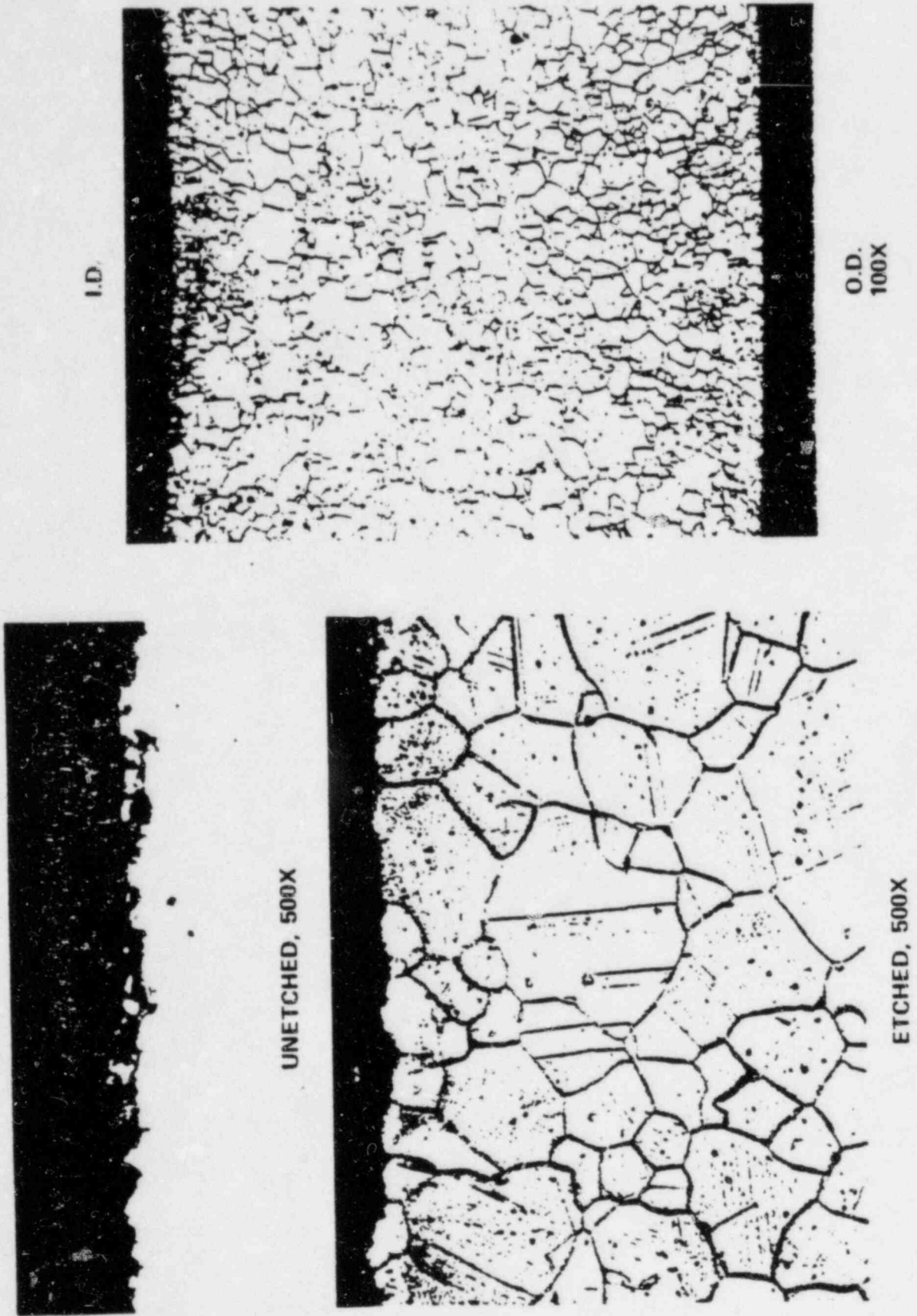
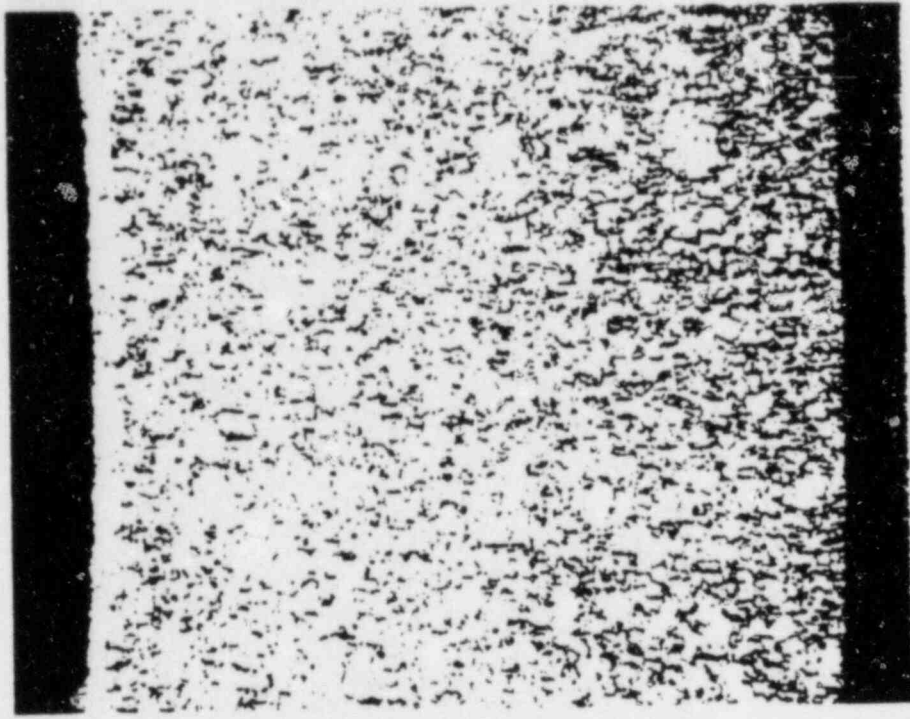


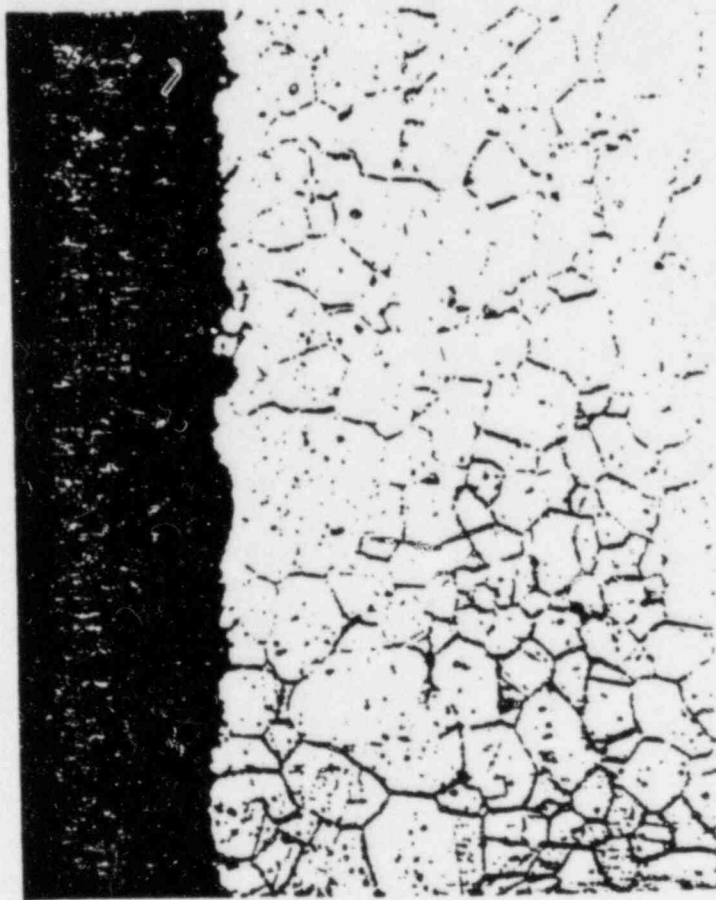
Figure 7.11. Micrograph of Specimen 2A2, I.D. Stressed Region After HFT



I.D.

O.D.

100X



500X

Figure 7.12. Micrograph of Specimen 2B2, I.D. Stressed Region After 1st Cycle

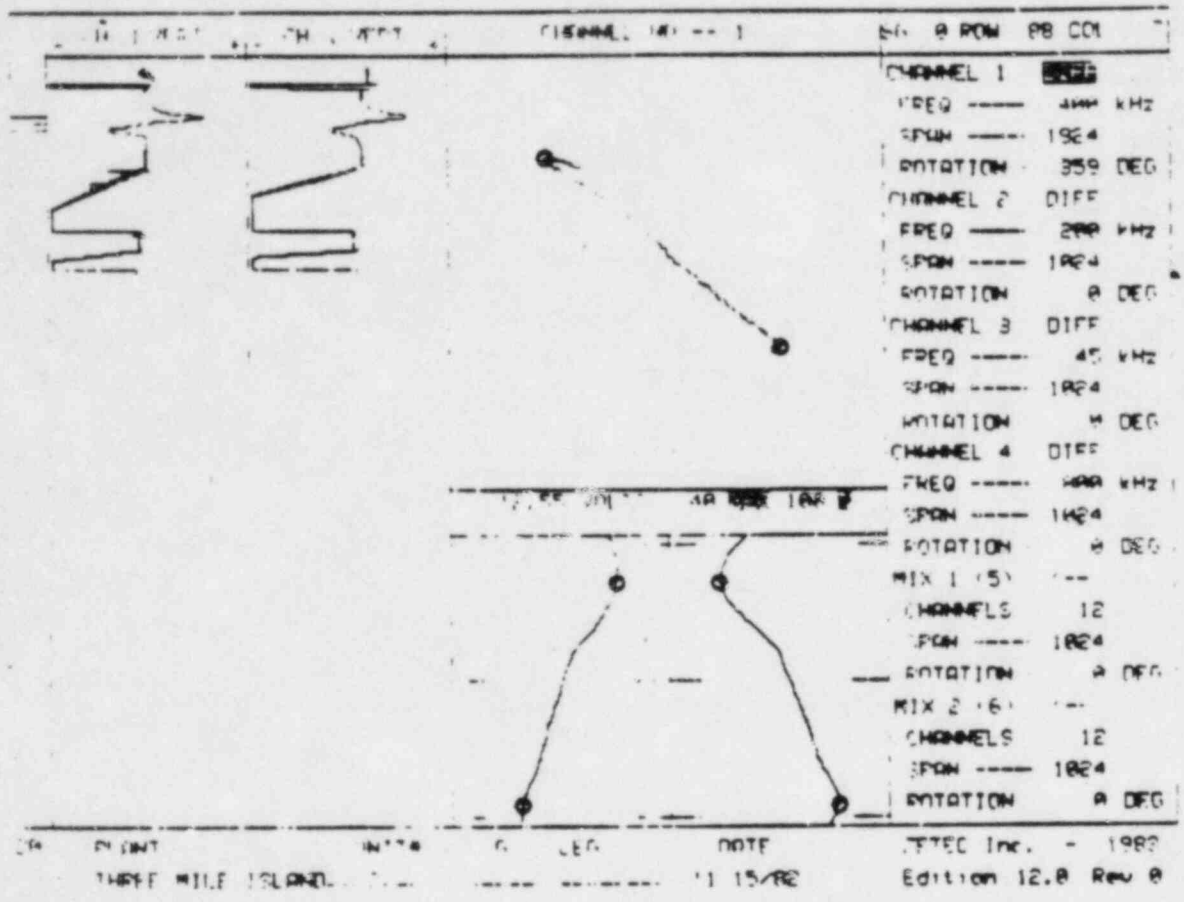


Figure 7-13. Thru-Wall Drill Hole (0.52 in) at 400 Khz.

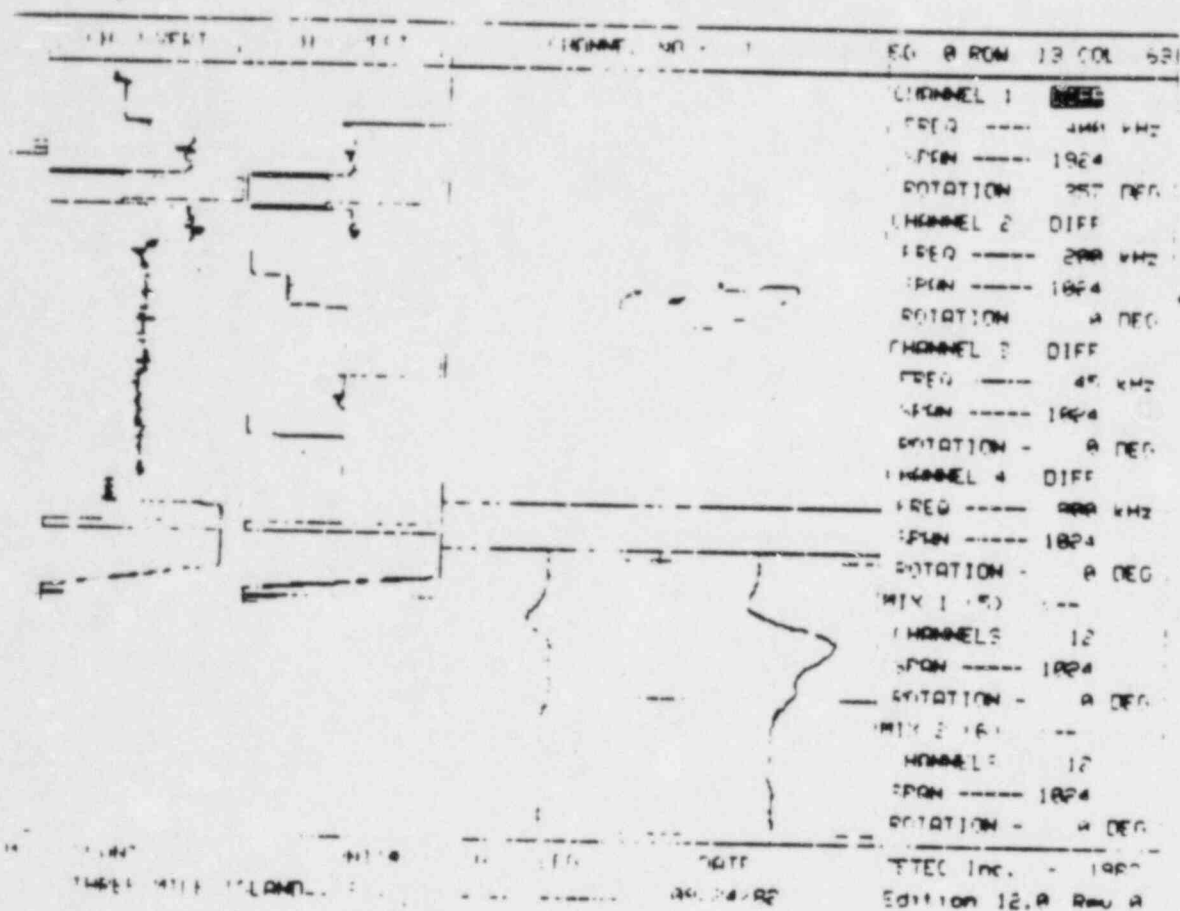


Figure 7-15 A13-63, 20 9/16"-23 9/16", Small Dent, 9/24/82

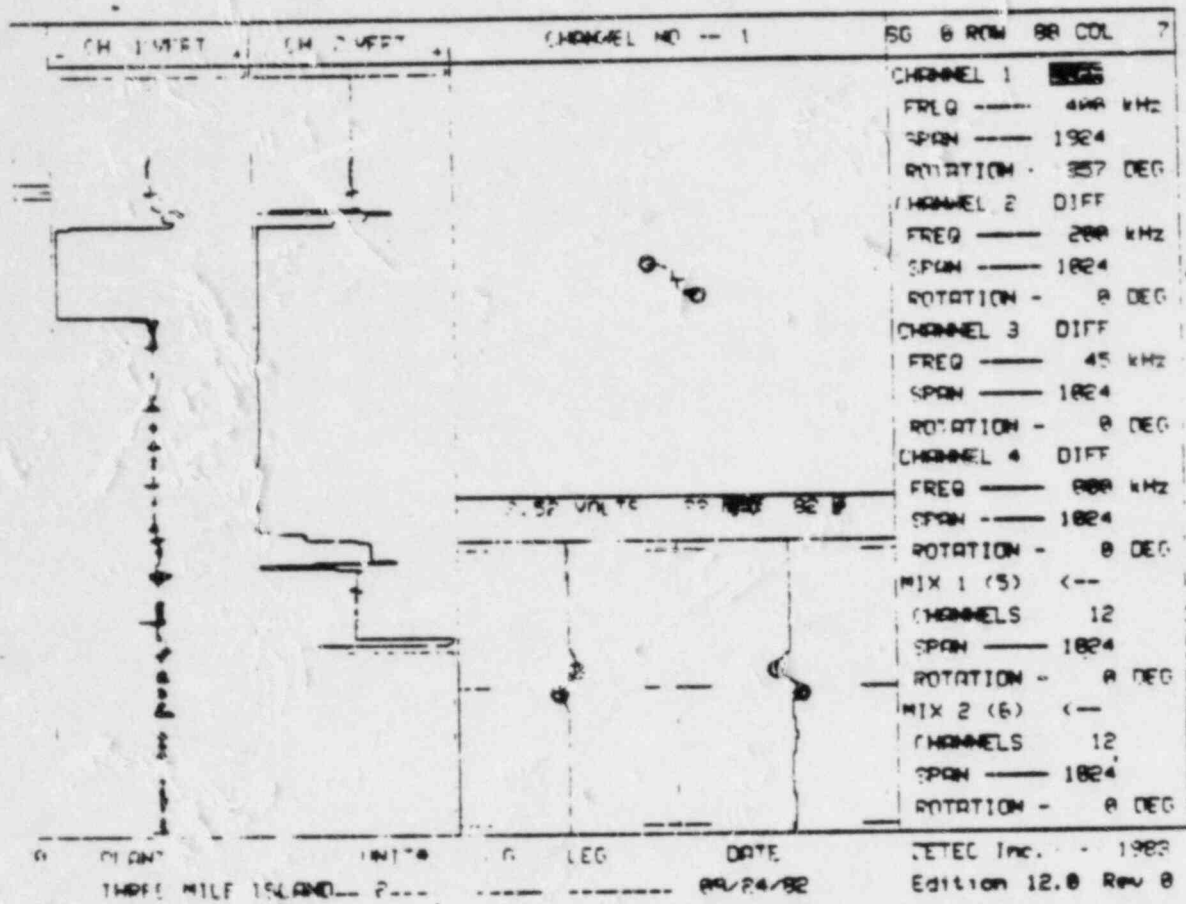


Figure 7-16 A88-7, 2"-9 3/4", 82% I.D., 9/24/82

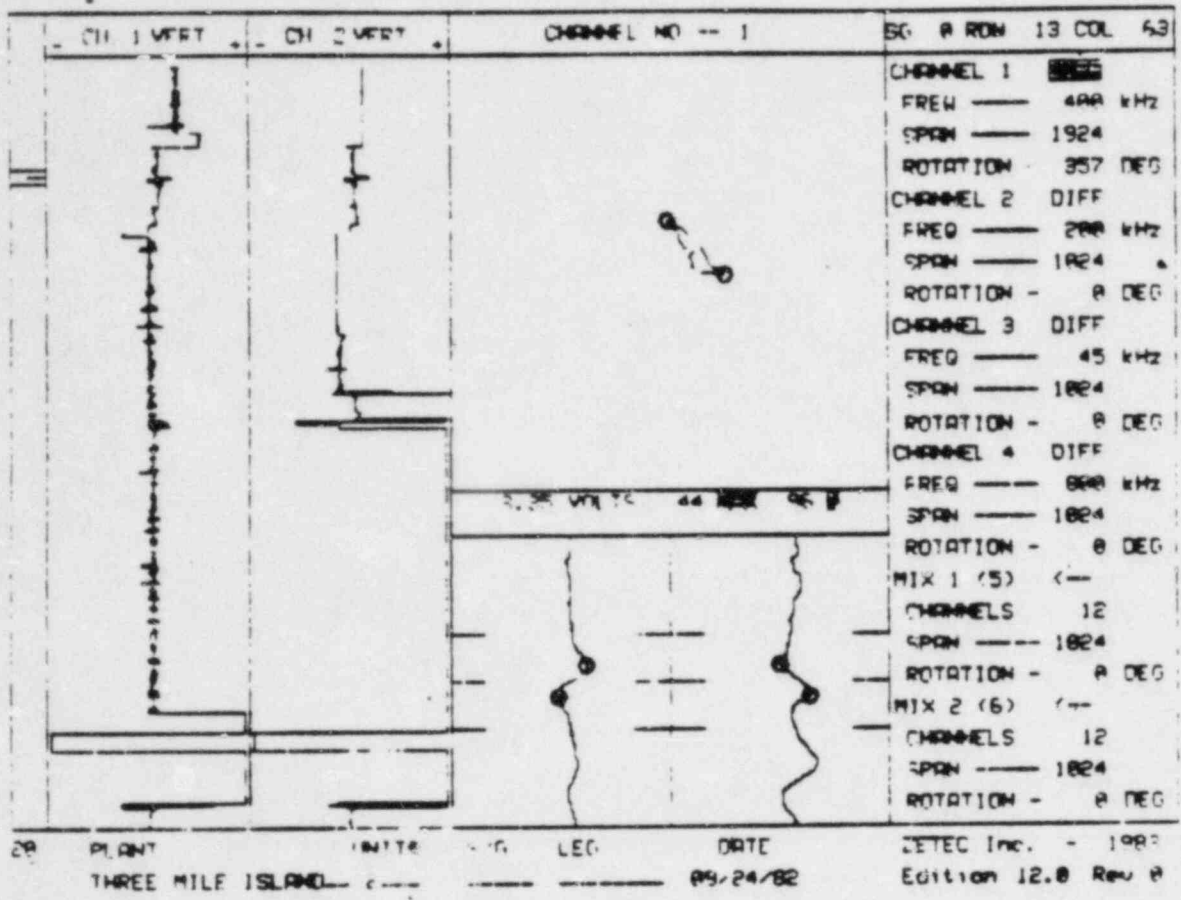


Figure 7-17 A13-63, 11"-20 9/16, 96% I.D., 9/24/82

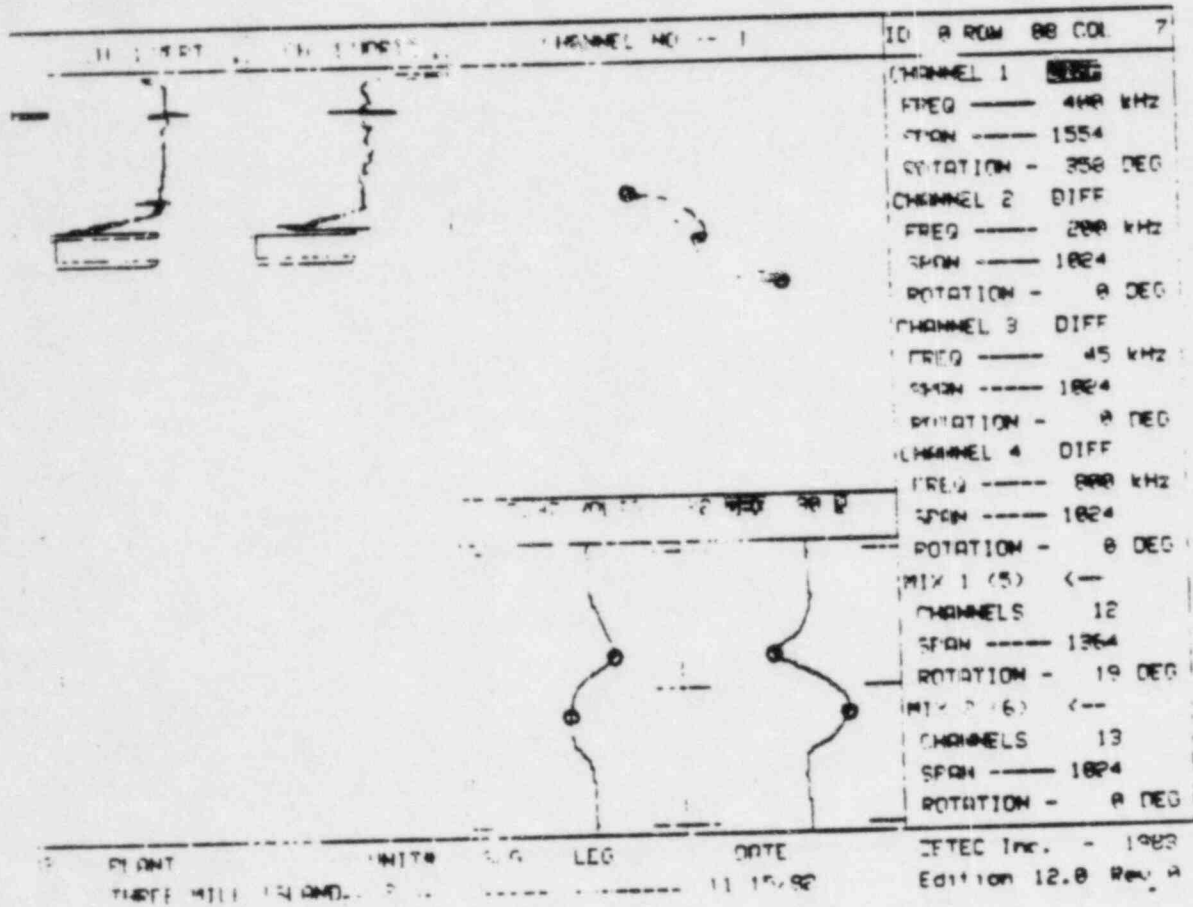


Figure 7-18 A88-7, 2"-9 3/4", 11/15/82

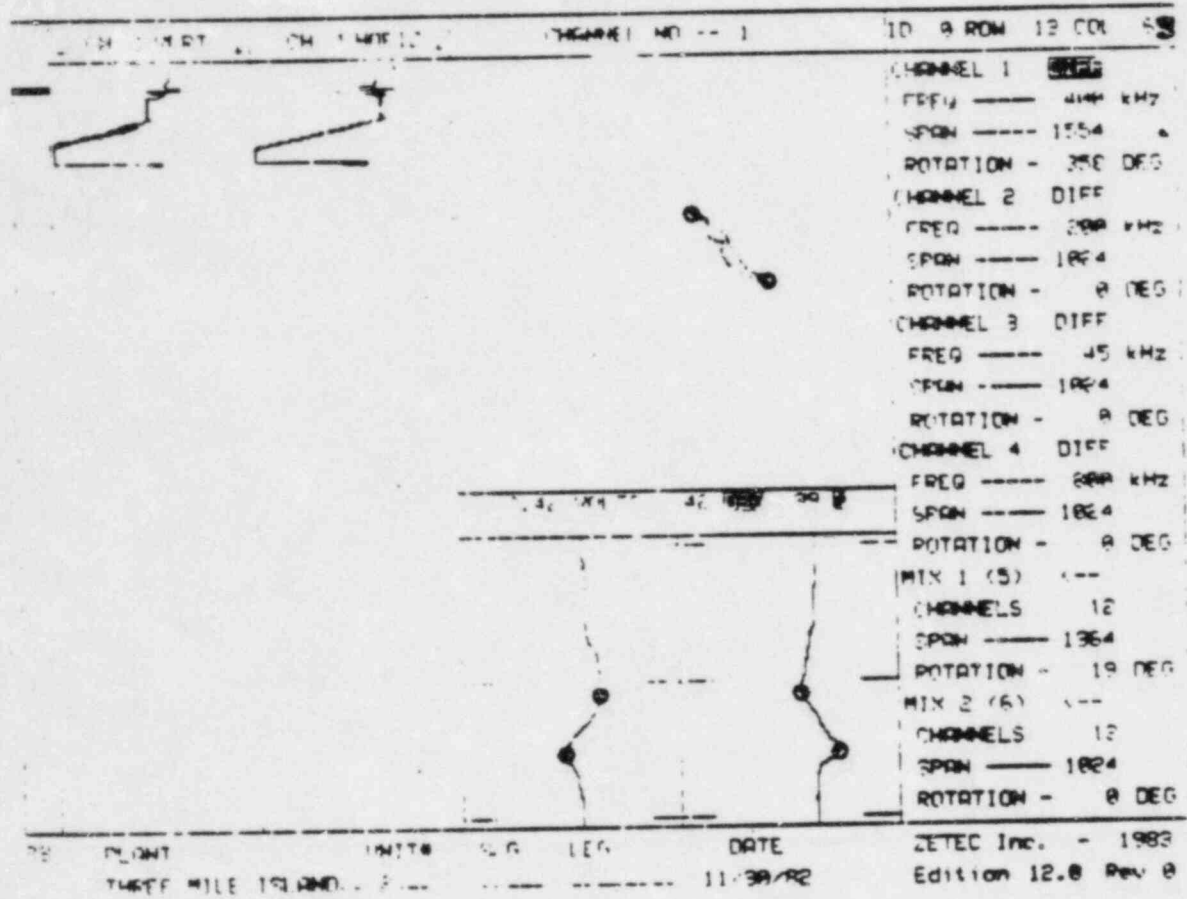


Figure 7-19 A13-63, 11" to 20 9/16" 11/30/82

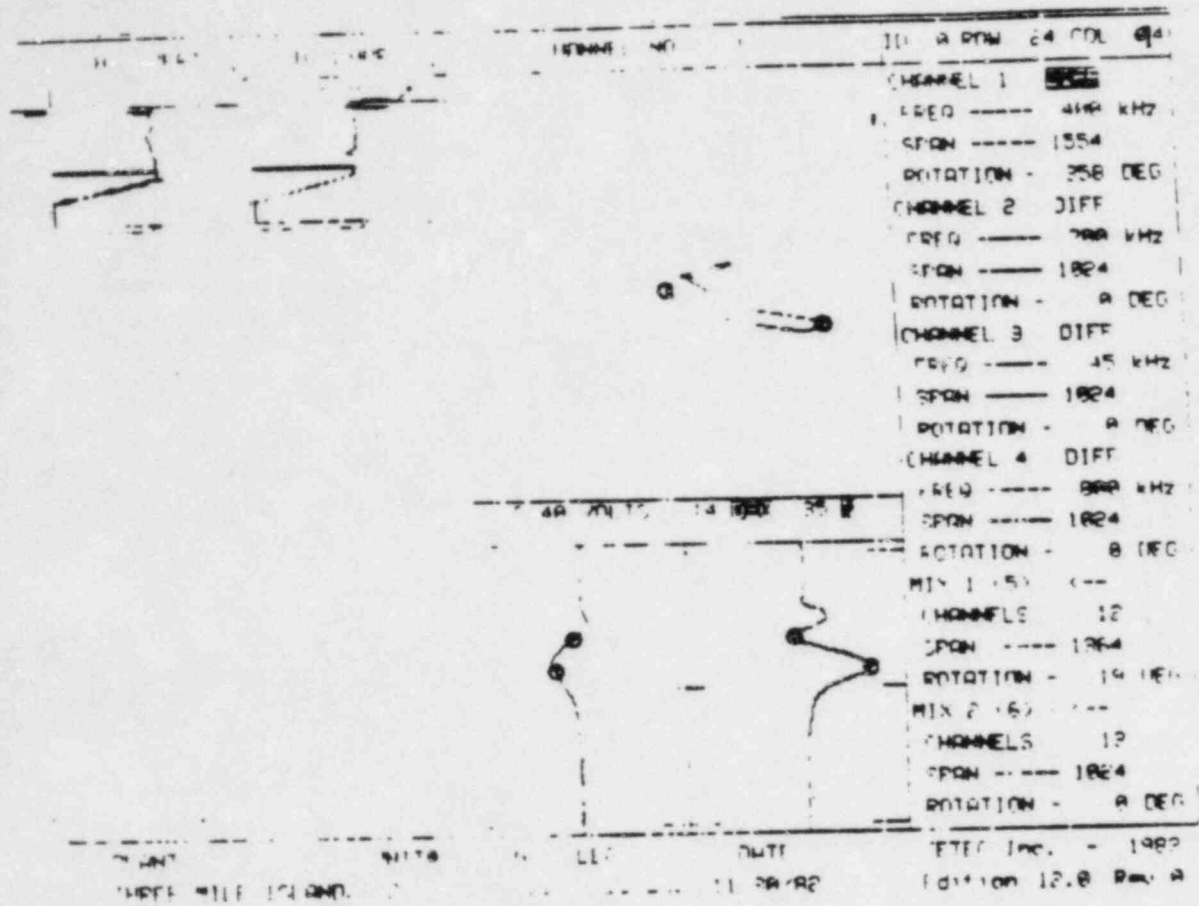


Figure 7-20, A24-94, 19 5/16" to 25 7/16" 11/30/82

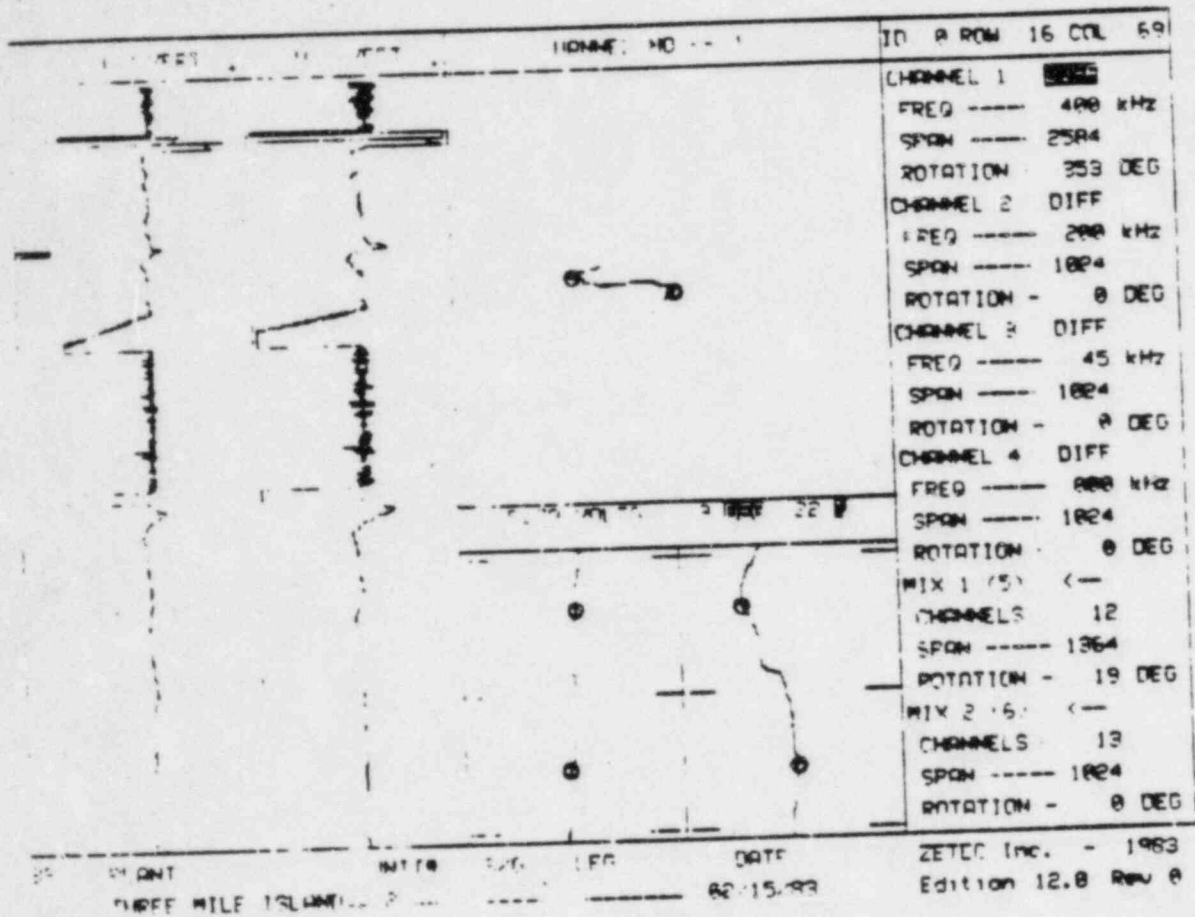


Figure 7-21 A 16-69, 6½"-12½" 2/15/83

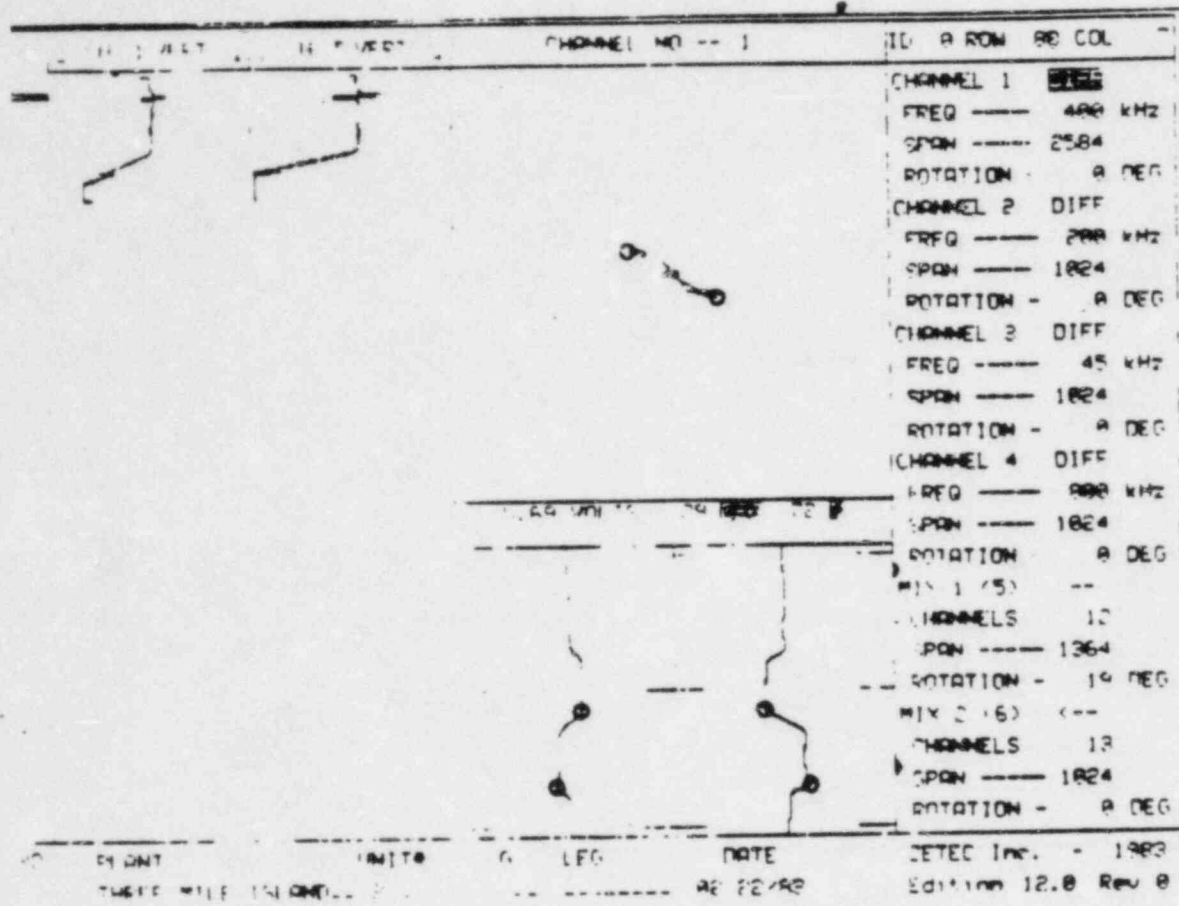


Figure 7-22 - A88-7, 2" to 9 3/4", 2/22/83

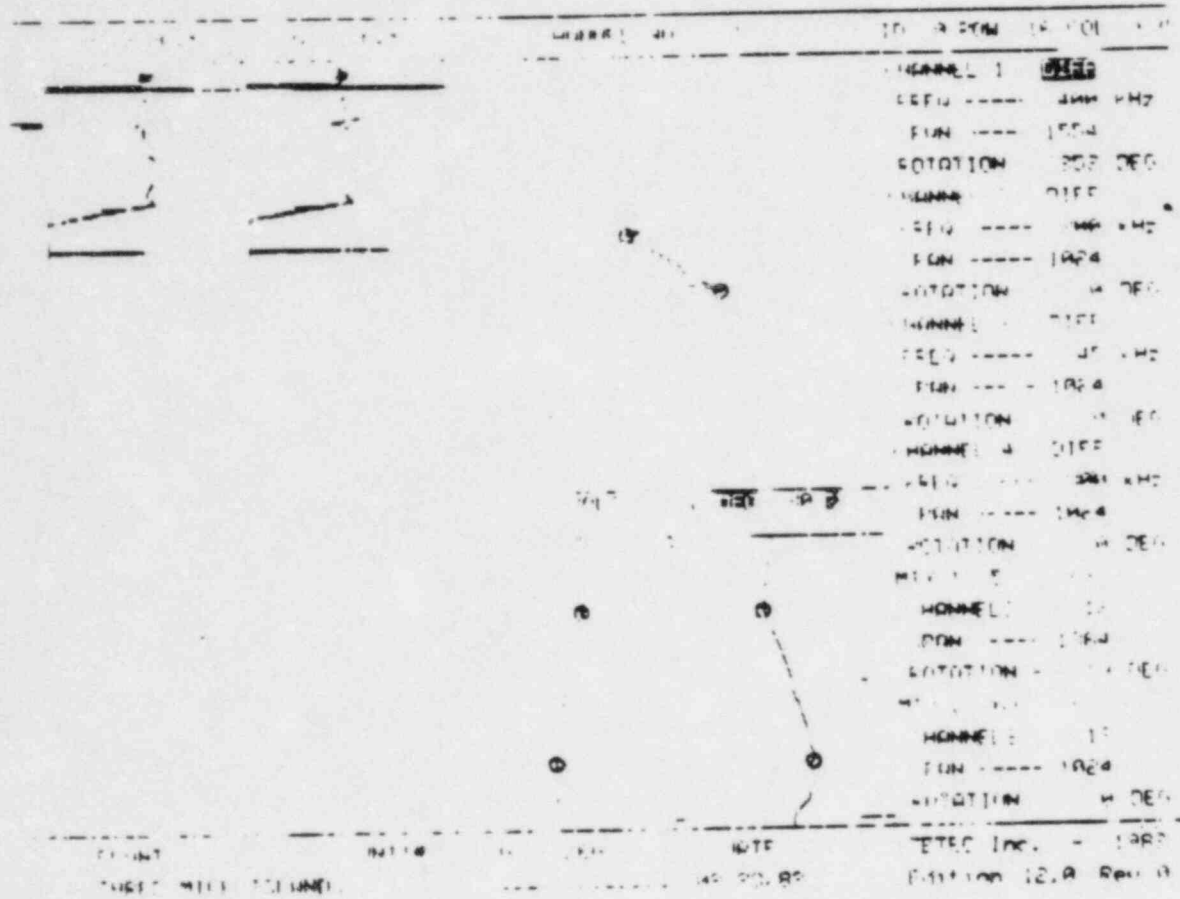


Figure 7-24 A16-69, 6½" to 12½" 3/23/83

TABLE 7-1

RESULTS OF VISUAL EXAMINATION OF C-RINGS - TEST #1

NUMBER	AFTER CYCLE	PITS								MECHANICAL MARKS		CRACKS		REMARKS	
		INCIPIENT		POSSIBLE		SHALLOW		DEEP		ID	OD	ID	OD		
		ID	OD	ID	OD	ID	OD	ID	OD	ID	OD	ID	OD		
1D2	HFT 1					X					X				OD-Spot of Bright Metal
1D1	HFT 1					X		X			X				
1B2	HFT 1								X		X	X			One Old Pit ID- Brown Spot & Mech. Pits
1B2	HFT 1					X					X	X			ID-Stains
2B5	1										X				OD-Light Colored
1A1	HFT 1					X					X	X			
1H3	HFT 1			X				X							Rust Color Pit-like Stains
1E2	HFT 1			X											Rust Color Pit-like Stains Stain
1E1	1crT 1			X											OK
2D1	HFT 1					X					X	X			OD-Patchy Oxide Corros. At a Pit?
2B1	HFT 1								X						
1A2	HFT					X					X				
2A1	HFT 1					X			X			X		X	(At a Pit Between Bolt & Edge) Cracklike Pit Between Bolt & Edge
1B4	PRE											X			Bright Gouges and Stains-ID

TABLE 7.2
RESULTS OF VISUAL EXAMINATION OF C-RINGS-TEST #2

NUMBER	AFTER CYCLE	PITS								MECHANICAL MARKS		CRACKS		REMARKS
		INCIPENT		POSSIBLE		SHALLOW		DEEP		ID	OD	ID	OD	
		ID	OD	ID	OD	ID	OD	ID	OD					
1E6	HFT 1													OK OK
1E5	HFT 1									X				OK
1E4	HFT 1									X				OK
1D3	HFT 1									X	X			OLD
2B3	HFT 1					X*			X	X		X		OD OK
1A4	HFT 1		X		X					X				
2D3	HFT 1					X				X	X			OLD MARKS
2D2	HFT 1					X				X	X			OLD
2B3	HFT 1				X									BRIGHT METAL PATCHES BRIGHT METAL&OXIDE PATCHES
2B2	HFT 1				X	X				X	X			BRIGHT METAL&OXIDE PATCHES
2A4	HFT 1				X					X	X			
2B4	PRE							X		X	X			RUSTY ID STAINS ID MECH. PIT
1A5	1									X				
2A2	HFT													

* Active

TABLE 7.3
RESULTS OF VISUAL EXAMINATION OF SPECIMENS AFTER PEROXIDE EXPERIMENT

NUMBER	CYCLE	PITS POSSIBLE		SURFACE		DEEP		MECHANICAL MARKS		CRACKS	REMARKS
		ID	OD	ID	OD	ID	OD	ID	OD		
P1D4	H ₂ O ₂										ID RUSTY
P1D5				*							ID RUSTY SOME OD
P1D3				*							ID RUSTY
P1D2				X							ID RUSTY
P2D1											GREY-BLACK
P1A5											GREY-BLACK
P1A4											OK
P1A3											OK
P1A1											ID DEBRIS
P1A2											OK
P2A5											OK
P2A3											OK
P2A4											OK
P2A2											OK
P2A1											OK
P2D2											OD WORM LIKE FEATURES

CORE MATERIALS - NO UNUSUAL OBSERVATIONS

* ACTIVE

Table 7-4
WEIGHT CHANGES OF EXPOSED C-RINGS

<u>Sample Number</u>	<u>Initial Weight</u> (gm)	<u>Final Weight</u> (gm)	<u>Weight Change</u> (mg)	<u>Last Cycle Completed</u>
P1A1	7.88915	7.88771	-1.44	H ₂ O ₂
P2A1	7.69279	7.69167	-1.12	H ₂ O ₂
1A2	7.81927	7.81571	-2.56	HFT
1B1	7.58345	7.58255	-0.9	1st
2A2	7.61330	7.61205	-1.25	HFT
2B2	7.47326	7.47159	-1.6	1st

TABLE 7-5

SUMMARY OF TUBE EDDY CURRENT INSPECTIONS

Date of Inspection	Tube	Section	Indication		Change From Previous Inspection		Comment
			ID.	OD.	YES	NO	
9/82	A24-94	25 7/16-30 13/16					Baseline Inspection
	B94-27	18-24½					
	B16-22	59-64					
	A16-69	2-6½		X			
	B111-62	237 5/8-240 5/8					
	A13-63	38 1/8-41 1/8					
	A13-63	20 9/15-23 9/16				Dent	
	A88-7	9 3/4-12 1/4					
	A13-63	11-20 9/16		X	X		
	B16-22	52-59					
	A37-29	35½-41½					
	B27-47	58-64					
	A37-29	29½-35½					
	B27-47	52-58					
	B113-62	31½-37½					
	A24-94	19 5/6-25 7/16			X		
	11/15/82	B16-22	52-59				
A88-7		9 3/4-12 1/4		X		X	
11/30/82	A24-94	19 5/16-25 7/16			X	X	After HFT
	A13-63	11-20 9/16		X	X	X	

TABLE 7-5 (Cont'd)

SUMMARY OF TUBE EDDY CURRENT INSPECTIONS

Date of Inspection	Tube	Section	Indication		Change from Previous Inspection		Comment
			ID.	OD.	YES	NO	
2/15/83	A24-94	36-42					Baseline Inspection
	B94-27	4½-10½	X				
	A16-69	6½x12¼	X				
	A88-7	9 3/4-12 1/4	X			X	
	B16-22	52-59				X	
3/2/83	A13-63	11-20 9/16	X	X			Post Cycle 1
	A24-94	19 5/16-25 7/16		X		X	
3/23/83	A16-69	6½-12¼	X			X	After H ₂ O ₂ Run
	B94-27	4½-10½				X	
	A24-94	36-42					

8.0 SUMMARY

Consistent with the objectives of the LTCT program, testing is in progress to monitor the long-term corrosion and stress corrosion performance of service-exposed TMI-1 OTSG tubing. Specimens in two "Lead Tests" have completed approximately six months of exposure to lithiated boric acid solutions, with compositions comparable to that of PWR primary coolant, in a refreshed autoclave system.

In addition to lithium hydroxide and boric acid, each test solution also contained low level contaminants consisting of Cl^- (~ 0.1 ppm as NaCl), F^- (~0.1 ppm as NaF) and sulfur containing species. Test 2 contained ~ 0.1 ppm SO_4^{2-} as Na_2SO_4 and Test 1 contained ~ 0.058 ppm $\text{S}_2\text{O}_3^{2-}$ as $\text{Na}_2\text{S}_2\text{O}_3$ (0.058 ppm $\text{S}_2\text{O}_3^{2-}$ is the molar equivalent of 0.1 ppm SO_4^{2-}).

The specimens in these tests have been subjected to operational sequences which parallel those encountered in normal plant operations. Each test has completed a HFT cycle and two Operations cycles. Although the lithium hydroxide and boric acid concentrations during successive cycles has been reduced to simulate plant practice due to core depletion, nominal contaminant levels have remained unchanged.

Specimens in the two lead tests consist of axially loaded tubes and C-rings stressed to place the ID surface in tension. Tube specimens were prepared from a TMI OTSG tube material both with and without in-plant generated defects. C-rings were prepared from both service exposed and archieve (non-service exposed), tubing material.

Metallographic examination of C-rings removed at the end of each cycle has shown no evidence of new defect formation attributable to the simulated plant exposure conditions. Likewise, periodic eddy current examination of the tube specimens has shown no indication of growth of defects existing prior to start of the test.

A 500 hour hydrogen peroxide clean-up exposure of other specimens was performed in a recirculating loop. Chemistry and operational conditions during the exposure paralleled those expected to be used during the peroxide clean-up of the TMI-1 primary system. Specimens in the H_2O_2 exposure consisted of axially loaded TMI OTSG tubes which had previously been explosively expanded into a collar (simulating the repair process for defected tubes in the upper tubesheet), an axially loaded tube, C-rings comparable to those in Tests 1 and 2, and U-bends prepared from materials used in other TMI-1 core components. Visual examination of all specimens following the peroxide exposure showed the existence of shallow pits on the ID surface of some of the C-rings.

These peroxide exposed specimens have been inserted in two additional once-through loops and will be subjected to chemical and operational conditions identical to those of "Lead Test No. 2". All four tests are currently in progress.

9.0 FUTURE WORK

Consistent with the program plan, Lead Tests 1 and 2 are continuing through four additional operations cycles. The test solution composition during these exposures will be established as outlined in Table 5-7. Likewise, the specimens which were exposed to the peroxide cleaning solution, have been placed in two additional tests which will follow the "Lead Test" format. These tests, Tests 3 and 4, have been started and will be subjected to a HFT and four Operations Cycles. Tests 1 and 2 will be placed on hold until the HFT cycle of Tests 3 and 4 are completed. All four tests will then be restarted at the same time and be maintained on the same operations schedule. This will make the eddy current and visual inspection shutdowns for all tests coincide. Completion of each Operations Cycle, including eddy current and visual examination of samples, should require approximately two calendar months.

Post-test metallography, as presently structured, shall consist of 48 samples selected for examination from those specimens remaining after the final test exposure. The option for examination of additional specimens shall remain open.

A second interim report will update the operations of Tests 1 and 2 and report on the initial exposures of Tests 3 and 4. Specifically, the second interim will contain data generated during Cycles 3 and 4 for Tests 1 and 2 and the HFT and Cycles 1 and 2 for Tests 3 and 4.

10.0 APPENDICES

10.1 Procedure for Loop Operations During Lead Test HFT Cycle.

The following procedure applies to operation during the HFT cycle of Lead Tests 1 and 2.

1. Fill the autoclave with make-up tank water for the appropriate test (No. 1 = thio-sulfate-dosed RCS, No. 2 = sulfate-dosed RCS). Leave some head space in the autoclave, after the sample train is loaded.
2. Sparge N_2 through the autoclave bulk, venting the N_2 (and whatever waer vapor it carried) out the top of the autoclave and into the radwaste drain line.
3. After sparging has proceeded for a standard interval, initiate pumping at 1120 psig.

Note: 1120 psig is the system pressure for all of the HFT phase only. (It corresponds to a pressure above the saturation pressure for 550°F, the maximum temperature of the HFT phase).

4. The autoclave will fill from pumping through the leak. When full, valve off sparge inlets and exits. The autoclave pressure will now rise to 1120 psig.
5. Apply 2260 psig total to the pressurization loading bellows. (This gives a ΔP between the bellows and the bulk of 1140 psi which, acting on the 0.44 in^2 area of the bellows, applies 500 lb. axial load on the samples).
6. Follow temperature cycles per GPU procedures, maintaining all 3 pressures (bellows, autoclave, and system) at the values given. Specific steps for 1120 psig system 1120 psig autoclave, and 2260 psig bellows, with constant flow are:

- (6a) Heat to $150 \pm 50^{\circ}\text{F}$ and hold 24 ± 8 hr.
- (6b) Heat to $550 \pm 5^{\circ}\text{F}$ at $(100^{\circ} \pm 50^{\circ})/\text{hr}$.
- (6c) Hold at $550 \pm 5^{\circ}\text{F}$ for 24 ± 8 hr.
- (6d) Cycle ($550 \pm 5^{\circ}\text{F}$) to $450 \pm 5^{\circ}\text{F}$) 4 times at $(100 \pm 50^{\circ}\text{F})/\text{hr}$.
- (6e) Hold at $550 \pm 5^{\circ}\text{F}$ for 1 week (minimum).

7. Initiate cooldown.

- (7a) Increase bellows pressure to 3620 ± 250 psig; that is to a range between 3370 psig MINIMUM and 3870 MAXIMUM. The lower end of the range is preferred to preclude overloading if the system pressure drops on cooling.

Note: The required sample load of $1100 \text{ lb} \pm 10$ percent (990 to 1210 lb) is achieved by a differential pressure between the bellows and the autoclave of 2500 ± 250 psi (2250 to 2750 psi). Example: 1120 psig autoclave + 2250 psi differential = 3370 psig bellows.

- (7b) Maintain 1120 psig in system and autoclave while still at $550 \pm 5^{\circ}\text{F}$.

- (7c) Cool to $130 \pm 5^{\circ}\text{F}$ at a rate of $(100 \pm 50^{\circ}\text{F})/\text{hr}$. (as far as practical). In practice this rate will prevail until about 225°F . Below 225°F , the maximum achievable rate should be instituted to reach $130 \pm 5^{\circ}\text{F}$ in 4 to 5 hours from 225°F .

- (7d) While cooling, close attention to the autoclave pressure is required and adjustments to the bellows pressure may be required must be compensate for rapidly by decreasing the bellows pressure so that the bellows pressure is always within the range of 2250 - 2750 psig greater than the autoclave pressure. In fact, the autoclave contents could become 2-phase on cooling if the contraction of autoclave water is not overcome rapidly enough by the pump rate through the leak, and the autoclave pressure will drop. When this happens, simply lower the bellows pressure so that it is not above 2750 psig more than the autoclave nor below 2250 psig more than the autoclave, and log all changes: time, temperature and pressures.

- (7e) At $130 \pm 5^{\circ}\text{F}$, maintain or restore the 1120 psig autoclave and system pressures followed by decreasing the bellows pressure to 2260 psig, while maintaining continuous circulation.
8. Maintain parameters of (7e) and
- (8a) Vent MUT H_2 overpressure
 - (8b) Sparge MUT solution with N_2 with continuous venting for a minimum of 15 minutes to purge H_2 from the gas space of the MUT.
 - (8c) Sparge air at atmosphere pressure into MUT
 - (8d) Maintain aerated MUT at atmospheric pressure
9. Circulate under conditions of (8d) for a minimum of 2 weeks, 1120 psig aqueous pressure, 2260 psig bellows pressure.
10. Depressurize all systems, stop circulations, open autoclave while warm (130°F) and remove samples for inspection.

10.2 Procedure for Loop Operations During the Lead Test Operations Cycles

The following procedure applies to operation during Operations cycles for Tests 1 and 2 which follow the HFT cycle in series.

1. Fill the autoclave with make-up tank water for the appropriate test (No. 1 = thio-sulfate-dosed RCS, No. 2 = sulfate-dosed RCS). Leave some head space in the autoclave, after the sample train is loaded.
2. Sparge N_2 through the autoclave bulk, venting the N_2 (and whatever water vapor it carries) out the top of the autoclave and into the radwaste drain line.
3. After sparging has proceeded for a standard interval, add 15 psig H_2 overpressure to the MUT and initiate pumping at 1760 psig.

Note: 1760 psig is the system pressure for all of the Operations Cycles. (It corresponds to a pressure above the saturation pressure for 600°F, the maximum temperature of the Operations Cycles.)

4. The autoclave will fill from pumping through the leak. When full, valve off sparge inlets and exits. The autoclave pressure will now rise to 1760 psig.
5. Apply 2900 psig total to the pressurization loading bellows. (This gives a ΔP between the bellows and the bulk of 1140 psi which, acting on the 0.44 in² area of the bellows, applies 500 lb. axial load on the samples.)
6. Follow temperature cycles per GPU procedures, maintaining all 3 pressures (bellows, autoclave, and system) at the values given. Specific steps for 1760 psig system, 1760 psig autoclave, and 2900 psig bellows, with constant flow are:
 - (6a) Heat to 150 \pm 50°F and hold 24 \pm 8 hr.
 - (6b) Heat to 600 \pm 5°F at (100° \pm 50°)/hr.
 - (6c) Hold at 600 \pm 5°F for 24 \pm 8 hr.
 - (6d) Cycle (600 \pm 5°F) to (500 \pm 5°F) 5 times at (100 \pm 50°F)/hr. Hold each endpoint temperature for 24 \pm 8 hrs.
 - (6e) Hold at 600 \pm 5°F for 2 weeks (minimum).
7. Initiate cooldown.
 - (7a) Increase bellows pressure to 4260 \pm 250 psig; that is to a range between 4010 psig MINIMUM and 4510 psig MAXIMUM. The lower end of the range is preferred to preclude overloading if the system pressure drops on cooling.

Note: The required sample load of 1100 lb \pm 10 percent (990 to 1210 lb) is achieved by a differential pressure between the bellows and the autoclave of 2500 \pm 250 psi (2250 to 2750 psi). Example: 1760 psig autoclave + 2250 psi differential = 4010 psig bellows.

(7b) Maintain 1760 psig in system and autoclave while still at 600 \pm 5°F.

(7c) Cool to 130 \pm 5°F at a rate of (100 \pm 50°F/hr (as far as practical). In practice this rate will prevail until about 225°F. Below 225°F, the maximum achievable rate should be instituted to reach 130 \pm 5°F in 4 to 5 hours from 225°F.

(7d) While cooling, close attention to the autoclave pressure is required and adjustments to the bellows pressure may be required if the autoclave pressure drops. Drops in the autoclave pressure must be compensated for rapidly by decreasing the bellows pressure so that the bellows pressure is always within the range of 2250 - 2750 psig greater than the autoclave pressure.

In fact, the autoclave contents could become 2-phase on cooling if the contraction of autoclave water is not overcome rapidly enough by the pump rate through the leak, and the autoclave pressure will drop. When this happens, simply lower the bellows pressure so that it is not above 2750 psig more than the autoclave nor below 2250 psig more than the autoclave, and log all changes: time, temperature and pressures.

(7e) At 130 \pm 5°F, maintain or restore the 1760 psig autoclave and system pressure followed by decreasing the bellows pressure to 2900 psig, while maintaining continuous circulation.

(7f) Maintain parameters of (7e) for a minimum of 1 week.

8. Reheat to (600 ± 5) °F and hold.

(8a) Heat to (600 ± 5) °F at (100 ± 50) °F/hr maintaining 1760 psig autoclave pressure and the required differential pressure on the bellows for the 500 lb load (see Step 5). Specifically, the bellows total pressure should always be between 2790 and 3010 psig (2900 psig nominal) for the autoclave pressure of 1760 psig (this gives the 1140 ± 110 psig differential bellows pressure of Step 5.

(8b) Hold at (600 ± 5) °F for 1 month minimum.

9. Initiate cooldown.

(9a) Repeat Steps (7a) and (7b).

(9b) Cool to ambient. Follow steps (7c) and (7d) except take temperature to ambient.

(9c) At ambient, repeat Step (7e), by restoring autoclave to 1760 psig if necessary and lowering bellows pressure to 2900 ± 110 psi. Maintain circulation.

10. Maintain conditions of (9c) and

(10a) Vent MUT H₂ overpressure.

(10b) Sparge MUT solution with N₂ with continuous venting for a minimum of 15 minutes to purge H₂ from the gas space of the MUT.

(10c) Sparge air at atmospheric pressure into MUT.

(10d) Maintain aerated MUT at atmospheric pressure.

11. Circulate under conditions of (10d) for a minimum of 2 days, 1760 psig aqueous pressures, 2900 psig bellows pressure.

12. Depressurize all systems, stop circulations, open autoclave and remove samples for inspection.

The above 12 steps cover the first Operations Cycle of GPU SP-1101-22-008, Rev. 1, on Lead Tests, their Paragraph 4.5.3.8, Steps 14-26.

GPU SP-1101-22-008, Rev. 1, Paragraph 4.5.3.8, Steps 27-30 are repeat operations. Each GPU step requires all 12 of the above Westinghouse steps, except that their Step 30 requires 2 of our 12 steps. Note from GPU SP-1101-22-008, Rev. 1, that the make up tank chemistry is the only variation from GPU step to step.

10.3 Methods for Preparation of Stock and Makeup Tank Solutions

For preparation of all solutions, except boric acid solutions, reagent grade chemicals will be used. Special Quality Grade* (Nuclear Grade) H_3BO_3 , with a maximum sulfate concentration of 0.00016 percent (1.6 ppm) will be used to prepare all boric acid solutions in the LTCT program. Weighings will be made on an analytical balance for all weights below 50g. Over 50 g, a top loading balance will be used.

Deionized water with a conductivity of $\sim 0.1 \mu\text{mho}$ (when deaerated) will be used for dilution.

Graduates and storage (holding) tanks will be of polyethylene.

One liter stock solutions, 1000 ppm in respect to the anion, will be volumetrically prepared for sodium fluoride, sodium chloride, sodium thiosulfate and sodium sulfate. The lithium hydroxide stock solution will be 5000 ppm in respect to lithium. Aliquot volumes will be pipetted from the stock solutions for individual make up tank solution preparations.

The orthoboric acid will be weighed and dissolved in approximately 20 l of demineralized water. This solution will be placed in a 50-l polyethylene

*U.S. Borax and Chemical Corp.

holding tank, along with the required aliquot volumes of the specified anion and cation stock solutions and diluted to 50 l with additional water. Due to problems associated with the loss of fluoride and hydrazine in the holding tanks, F^- , hydrazine, and Cl^- will be added to the MUT during the transfer process just prior to test startup.

The 50 l test solution will be deaerated (and mixed) by sparging with nitrogen; the sparging tube (stainless steel or Inconel 600), of sufficient length to extend to the bottom of the tank, will be manually swirled several times to compliment the mixing by sparging. The 50 l of solution will be stored under continuous nitrogen sparging in the holding tank until ready for use. A minimum of 4 hours of sparging is required to provide mixing and deaeration of the solution.

10.3.1 Preparation of Stock Solutions

Lithium Hydroxide (LiOH)

Dissolve 30.2262 g $LiOH \cdot H_2O$ in deionized water in a 1-l polyethylene volumetric flask, and add sufficient water to make 1.0 l. LiOH will be weighed on an analytical balance. Lithium concentration is 5000 ppm. Solution will be stored in a polyethylene bottle.

Sodium Fluoride (NaF)

Dissolve 2.2102 g. NaF (weighed on an analytical balance) in a 1-l polyethylene volumetric flask partially filled with deionized water; add sufficient water to make 1.0 l. The solution will be stored in a polyethylene bottle. The fluoride concentration is 1000 ppm.

Sodium Chloride (NaCl)

Dissolve 1.6485 g NaCl (weighed on an analytical balance) in a 1-l polyethylene volumetric flask, partially filled with deionized water. Add water to make 1.0 l. The solution will be stored in a polyethylene bottle. The chloride concentration is 1000 ppm.

Sodium Thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$)

Dissolve 1.2918 g $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ (weighed on an analytical balance) in a 1-l polyethylene volumetric flask partially filled with deionized water. Add enough water to make 1.0 l. The solution will be stored in a polyethylene bottle. The solution will contain an equivalent of 1000 ppm SO_4^{2-} .

Sodium Sulfate ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$)

Dissolve 3.3540 g $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ (weighed on an analytical balance) in a 1-l polyethylene volumetric flask partially filled with deionized water. Add enough water to make 1.0 l. The solution will be stored in a polyethylene bottle. The SO_4^{2-} concentration is 1000 ppm.

10.3.2 Lead Test Solutions

HFT Solution 1 = Thiosulfate dosed RCS.

HFT Solution 2 = Sulfate dosed RCS.

Weigh 672.1 g orthoboric acid (2350 ppm B equivalent) for each Solution.

- * Dissolve in 20 l deionized water and place in 50-l polyethylene storage tank for each Solution.

add 5 ml stock (1000 ppm equivalent SO_4) $\text{Na}_2\text{S}_2\text{O}_3$ solution
to Solution 1 only.

add 5 ml stock (1000 ppm SO_4) $\text{Na}_2\text{S}_2\text{O}_4$ solution to Solution 2
only.

add 23 ml stock (5000 ppm Li) LiOH solution to each Solution.

- * Add sufficient deionized water (~30 l) to bring total volume up to 50 l for each Solution.

Add 0.7210 g of 65 percent aqueous hydrazine solution, 5 ml stock (1000 ppm F) NaF solution, and 5 ml stock (1000 ppm Cl) NaCl solution to the in-line addition vessel prior to solution transfer from the storage tank to the MUT.

Calculated solution concentration (ppm):

B = 2350

Li = 2.3

F = 0.1

Cl = 0.1

SO_4 = 0.1

** Hydrazine = 6

- * Sufficient water will be used initially to dissolve easily the orthoboric acid. Enough additional water (~30 l) will be added to attain the 50 l desired volume.

** Target value. Permissible range = 2-10 ppm.

10.3.3 Lead Test Operations Cycle Solutions

Cycle 1

weigh 343.2 g orthoboric acid for each Solution.

*Dissolve in 20 l deionized water and place in 50-l polyethylene holding tank for each Solution.

add 5 ml stock (1000 ppm SO_4) $\text{Na}_2\text{S}_2\text{O}_3$ solution to Solution 1 only.

add 5 ml stock (1000 ppm SO_4) Na_2SO_4 solution to Solution 2 only.

add 23 ml stock (5000 ppm Li) LiOH solution to each Solution.

*Add sufficient deionized water (~30 l) to bring total volume to 50 l for each solution.

Add 0.7210 g of 65 percent aqueous hydrazine solution, 5 ml stock (1000 ppm F) NaF solution and 5 ml stock (1000 ppm Cl) NaCl solution to the in-line addition vessel prior to solution transfer from the storage tank to the MUT.

Calculated solution concentration (ppm):

B = 1200

Li = 2.3

F = 0.1

Cl = 0.1

SO_4 = 0.1

** Hydrazine = 6

** Target value. Permissible range = 2-10 ppm.

Cycle 2

- Weigh 286 g orthoboric acid for each Solution.
- *Dissolve in 20 l deionized water and place in 50-l polyethylene holding tank for Solution 1 and Solution 2.
 - add 5 ml stock (1000 ppm F) NaF solution to each Solution.
 - add 5 ml stock (1000 ppm Cl) NaCl solution to each Solution.
 - add 5 ml stock (1000 ppm SO₄) Na₂S₂O₃ solution to Solution 1 only.
 - add 5 ml stock (1000 ppm SO₄) Na₂SO₄ solution to Solution 2 only.
 - add 18.5 ml stock (5000 ppm Li) LiOH solution to each Solution.
- *Add sufficient deionized water (~30 l) to bring total volume to 50 l for each Solution.

Add 0.7210 g of 65 percent aqueous hydrazine solution, 5 ml stock (1000 ppm F) NaF solution and 5 ml stock (1000 ppm Cl) NaCl solution to the in-line addition vessel prior to solution transfer from the storage tank to the MUT.

Calculated solution concentration (ppm):

- B = 1000
- Li = 1.85
- F = 0.1
- Cl = 0.1
- SO₄ = 0.1
- ** Hydrazine = 6

** Target value. Permissible range = 2-10 ppm.

Cycle 3

Weigh 143 g orthoboric acid for each Solution.

*Dissolve in 20 l deionized water and place in 50-l polyethylene holding tank for each Solution.

add 5 ml stock (1000 ppm SO_4) $\text{Na}_2\text{S}_2\text{O}_3$ solution to Solution 1 only.

add 5 ml stock (1000 ppm SO_4) Na_2SO_4 solution to Solution 2 only.

add 11.5 ml stock (5000 ppm Li) LiOH solution to each Solution.

*Add sufficient deionized water (~30 l) to bring total volume to 50 l for each Solution.

Add 0.7210 g of 65 percent aqueous hydrazine solution, 5 ml stock (1000 ppm F) NaF solution and 5 ml stock (1000 ppm Cl) NaCl solution to the in-line addition vessel prior to solution transfer from the storage tank to the MUT.

Calculated solution concentration (ppm):

B = 500

Li = 1.15

F = 0.1

Cl = 0.1

SO_4 = 0.1

** Hydrazine = 6

** Target value. Permissible range = 2-10 ppm.

Cycle 4, Cycle 5, Cycle 6

Weigh 28.598 g orthoboric acid for each Solution.

*Dissolve in 20 l deionized water and place in 50-l polyethylene holding tank for each Solution.

add 5 ml stock (1000 ppm SO_4) $\text{Na}_2\text{S}_2\text{O}_3$ solution to Solution 1 only.

add 5 ml stock (1000 ppm SO_4) Na_2SO_4 solution to Solution 2 only.

add 8.5 ml stock (5000 ppm Li) LiOH solution to each Solution.

*Add sufficient deionized water (~30 l) to bring total volume to 50 l for each Solution.

Add 0.7210 g of 65 percent aqueous hydrazine solution, 5 ml stock (1000 ppm F) NaF solution and 5 ml stock (1000 ppm Cl) NaCl solution to the in-line addition vessel prior to solution transfer from the storage tank to the MUT.

Calculated solution concentration (ppm):

B = 100

Li = 0.85

F = 0.1

Cl = 0.1

SO_4 = 0.1

** Hydrazine = 6

** Target value. Permissible range = 2-10 ppm.

10.4 Procedures Used During Hydrogen Peroxide Test Operations

10.4.1 Test Loop Operations

1. Prepare 50 L of a deoxygenated solution with the nominal test composition (2350 \pm 50 ppm B, 2.0 \pm 0.2 ppm LiOH, 100 \pm 50 ppb SO_4^{2-} and pH 8.1 \pm 0.1 adjusted with ammonia) and transfer to the MUT using standard methods already established for these operations. Prepare an additional batch of 4 L (or more) for filling autoclaves (Step 6).

NOTE: From this point on in the test procedure it is important to accurately measure and record the volume of all solutions either added to or removed from the loop. All residual analytical chemistry samples should be retained following the analysis, with an analytical chemistry procedure record of how much (volume or weight) of the submitted sample was actually consumed by the analytical procedure. Any other effluent samples (for pH, etc.) should also be retained. A record should be kept of the amount of solution added to the MUT and the time of addition.

2. Sparge the MUT for the standard time interval to assure that the solution is deoxygenated.
3. Initiate flow through the bypass leg (with specimens isolated) at maximum flowrate.
4. Maintain maximum flow conditions and sample the MUT hourly until two successive samples show that the pH and conductivity are stable - pH within specified range and measured conductivity remains ± 2 μmho . Make additions of the ammonium hydroxide stock solution, as required, to maintain pH in specified range.
5. Sample the MUT for determination of baseline SO_4 level by IC.

6. Fill the autoclaves with the additional makeup solution of Step 1 and pipe in the sample stringers. Note that the sample stringers go in test with the "as-is" inside surface condition (no pre-test rinsing or flushing). Maintain sample inlet and outlet valves closed and bypass valves open at this step, leaving air in the sample stringers.
7. Prior to initiating flow through the specimens, set the back pressure regulator in the pressure relief/drain line of each autoclave at 400 psig and heat autoclave to $130 \pm 5^{\circ}\text{F}$.
8. Initiate recirculation flow through the specimens at the maximum flow rate achievable. The entrapped air in the specimens will be pushed out and on into the makeup tank.
9. Adjust and balance temperature-flow values using heating tapes, and - if necessary - flowrate adjustments.
10. For the autoclave containing the 2 repair test specimens, apply 1155 psig total pressure to the bellows. (This gives a ΔP between the bellows and the autoclave bulk, which is at atmospheric pressure of 1140 psi, which, acting on the 0.44 in^2 area of the bellows, applies 500 lb axial load on the samples).
11. For the autoclave containing the full section lead test specimen, the autoclave may begin to fill with primary solution through a possible leak. If this occurs, autoclave pressure will rise to 320 psig. The bellows pressure should then be increased to 1460 psig total bellows pressure (this gives a ΔP between the bellows and the autoclave bulk of 1140 psi which produces a 500 lb axial load on the sample. If the 400 psig primary pressure is insufficient to cause a primary to secondary leak, the bellows pressure should be set at 1155 psig as in Step 10.
12. Using the value of the solution volume in the loop (see Step 1), add the required volume of the hydrogen peroxide stock solution to the MUT by way of the addition bomb to produce a MUT concentration of 20 ppm.

Ten minutes after the peroxide addition, sample the MUT to verify that the desired peroxide concentration has been achieved. If peroxide concentration is not correct, continue to circulate and adjust peroxide.

13. When stable peroxide concentration, flowrate, and temperature are achieved on both systems, the 500 hour cleaning cycle has begun. Sample the MUT and autoclave effluent and determine pH and H_2O_2 concentration.
14. Until the H_2O_2 consumption rate and the stability of the pH is determined, sample the MUT and autoclave effluent hourly* and perform H_2O_2 concentration and pH measurements. Measure and record the data, hour and volume of all flushing and sampling volumes and of all volumes of additions to the loop, and maintain a continuous current record of the volume of solution in the loop for the entire duration of the test.
15. After conditions have stabilized and/or consumption rates have been determined, institute the reduced frequency of analyses which insures that 15-20 ppm H_2O_2 is maintained in the MUT. Continue the operations for the remainder of the 500 hour test.

10.4.2 Procedure for H_2O_2 Analysis Using Peroxide Kit HP-50

Test Method. The HP-50** kit employs the reagent ammonium thiocyanate plus ferrous iron in acid solution to give a red-orange color with hydrogen peroxide. The test is based on the oxidation of ferrous iron to ferric iron by peroxide with the formation of the intensely colored ferric thiocyanate complex.

*At the beginning of the test cycle, peroxide analyses of effluents should be conducted more frequently than hourly, until it is established that the hourly rate is sufficiently frequent to track peroxide consumption.

** CHEMetrics, Inc., Warrenton, Va.

Sample Preparation.

1. Measure 5.0 ml of loop water into the "snap-cup" using the precalibrated sampling syringe.
2. Add two drops of 20 weight percent sulfamic acid solution.
3. Dilute to 25 ml with distilled water.

NOTE: Each sample to be analyzed with this kit must be diluted, as above, prior to analysis with the kit.

Analysis Procedure.

1. Insert the ampoule tip into one of the four depressions at the bottom of the snap-cup and squeeze the ampoule toward the side of the cup. This movement will break the ampoule tip. The sample fluid will fill the ampoule, mix with the reagent, and form a colored solution whose intensity corresponds to the concentration of peroxide. A small bubble will remain in the tube.
2. Remove the ampoule and cover the tip with a finger. Invert the CHEMet several times, allowing the bubble to travel from end to end each time. (A protective cot may be used to prevent skin puncture.)

Use the appropriate comparator to determine the level of peroxide in the sample.

Readings should be taken no longer than 30 seconds after the CHEMet has been fired.

10.4.3 Procedure for Preparation of 50,000 ppm H₂O₂ Stock Solution.

1. Measure out 150 cc of 30 percent H₂O₂* (0.334 g H₂O₂/ml) solution.

*DuPont "Perone" 30 EG Hydrogen Peroxide.

2. Quantitatively transfer to a 1 liter polyethylene volumetric flask, and dilute to one liter. Stopper and invert several times to assure mixing is complete.
3. Using a micropiet transfer 50 μ l of the solution prepared in step 2 to another polyethylene volumetric flask, and dilute to one liter. Stopper and mix. (The concentration of this solution should be 2.5 ppm H_2O_2).
4. Analyze the solution prepared in Step 3 using the CHEMetrics hydrogen peroxide analysis kit.
5. Calculate the concentration of the stock solution prepared in Step 2 using the following expression:

$$C_s = \frac{C_m \cdot 1000}{C_s}$$

where

- C_s = the concentration of the H_2O_2 stock solution in ppm,
 C_m = the H_2O_2 concentration determined by use of the CHEMetrics H_2O_2 analysis kit (Step 4)
 V_s = the volume of the stock solution used to prepare the solution in Step 3.

6. Label the stock solution prepared in Step 2 with the date and the concentration calculated in Step 5.
7. At least once each week, redetermine the concentration of the stock solution by the procedure described in Steps 3 through 6.

NOTE: Since hydrogen peroxide will decompose in bright light, store the stock solution in a dark place when not being used.

10.4.4 Procedure for the Addition of Ammonium Hydroxide to the Loop

1. Withdraw 500 ml of solution from the loop using the effluent sample tap.
2. Adjust loop flow so that the chemical addition bomb is isolated.
3. Pressurize the sampling bomb from the top within nitrogen. The pressure applied must be greater than the pressure in the MUT.
4. Open the valve at the bottom of the bomb to allow any solution in the bomb to be forced into the MUT. The bomb will be empty when pressure in the MUT begins to rise. At that point close the valve at the bottom of the bomb.
5. Bleed the MUT nitrogen pressure back to the amount maintained during normal operations.
6. Shut the valve at the top of the addition bomb and disconnect the nitrogen supply.
7. Connect the vacuum source to the valve at the top of the addition bomb. Open the valve and begin to evacuate the bomb.
8. Calculate the volume of concentrated ammonium hydroxide (14 M) required to increase the loop pH by using the titration curve (Figure 10-1) and the following formula:

$$V_A = 2 V_L (ml_{\text{desired pH}} - ml_{\text{present pH}})$$

where,

- V_A = The volume of 14 M NH_4OH (ml) to be added,
 V_L = The volume (liters) of solution in the loop,
 $ml_{\text{desired pH}}$ = the reading derived from Figure 1 which corresponds to the desired pH,

$m_{\text{present pH}}$ = the reading derived from Figure 1 which corresponds to the present pH.

NOTE. To avoid adding excess NH_4OH and producing a higher pH than desired, adjustments should initially be made to the bottom of the 8.0 to 8.2 pH control range. After experience with the system and the procedure is achieved, adjustment to the middle of the pH range should be attempted.

9. To ~250 ml of the solution removed from the loop in step 1), add the volume of the 14 M NH_4OH solution calculated in step 8).
10. Shut the valve at the top of the chemical addition bomb, and suck the solution containing the NH_4OH into the bomb by opening the valve at the bottom of the bomb.
11. When all of the NH_4OH containing solution has entered the bomb, rinse the container with the remaining 250 ml of loop solution from step 1), and suck this solution into the sampling bomb.
12. Make sure that addition valves at the top and bottom of the bomb are closed, then divert loop flow through the bomb and flush bomb contents into the MUT.
13. Allow 15 minutes to assure mixing and then sample the MUT. Determine pH to assure that the desired increase has been achieved.

10.4.5 Procedure for the Manual Addition of Hydrogen Peroxide to the Loop

1. Withdraw 500 ml of solution from the loop using the effluent sample tap.
2. Adjust loop flow so that the chemical addition bomb is isolated.
3. Pressurize the sampling bomb from the top with nitrogen. The pressure applied must be greater than the pressure in the MUT.

4. Open the valve at the bottom of the bomb to allow any solution in the bomb to be forced into the MUT. The bomb will be empty when pressure in the MUT begins to rise. At that point close the valve at the bottom of the bomb.
5. Bleed the MUT nitrogen pressure back to the amount maintained during normal operations.
6. Shut the valve at the top of the addition bomb and disconnect the nitrogen supply.
7. Connect the vacuum source to the valve at the top of the addition bomb. Open the valve and begin to evacuate the bomb.
8. Calculate the amount of the H₂O₂ stock solution (nominally 50,000 ppm) required to change the loop concentration to the desired amount using the following expression:

$$V_A = \frac{\Delta C \cdot V_L}{C_S}$$

where,

- V_A = the volume of stock solution (liters) to be added to the loop,
 - ΔC = the desired increase in loop H₂O₂ concentration, in ppm,
 - V_L = the volume, in liters, of solution in the loop,
 - C_S = the concentration of the H₂O₂ stock solution, in ppm.
9. To ~250 ml of the solution removed from the loop in step 1), add the volume of the H₂O₂ solution calculated in step 8).
 10. Shut the valve at the top of the chemical addition bomb, and suck the solution containing the H₂O₂ into the bomb by opening the valve at the bottom of the bomb.

11. When all of the peroxide containing solution has entered the bomb, rinse the container with the remaining 250 ml of loop solution from step 1), and suck this solution into the sampling bomb.
12. Make sure that addition valves at the top and bottom of the bomb are closed, then divert loop flow through the bomb and flush bomb contents into the MUT.
13. Allow 15 minutes to assure mixing and then sample the MUT. Analyze for H_2O_2 to assure that the desired H_2O_2 concentration has been achieved.

NOTE: Hydrogen peroxide additions to the loop should only be made when loop pH is >7.0 to avoid decomposition.

10.4.6 Procedure for Loop Shutdown

1. At the completion of the 500 hour peroxide exposure (4:20 p.m. on March 15, 1983), sample the make-up tank (MUT) solution for (a) peroxide analysis, and (b) ion chromatographic sulfate analysis.
2. Terminate peroxide additions.
3. Retain 500 pound load on specimens and de-energize all loop heaters.
4. While maintaining flow through the specimens at the specified test flowrate, sample the MUT solution hourly and analyze for peroxide for the initial 2-3 hours of the cooldown period.
5. Maintain flow through the specimens overnight. Twenty-four hour surveillance during the cooldown is not required. However, prior to leaving the laboratory for the evening, sample the MUT for peroxide and sulfate analyses.

6. On the following morning, again sample the MUT for peroxide and sulfate analyses.
7. Terminate flow and reduce pressure on both the bellows and the remainder of the loop system.
8. Drain the contents of each autoclave into separate labeled containers and retain for further analysis at a later time.
9. Open the autoclaves, disconnect the sample train, and drain solution from each sample train into separate, appropriately labeled containers. Set aside for further analysis at a later time.
10. Transfer specimens to appropriate location for post-test examinations.
11. Drain MUT and remainder of loop into labeled containers. Retain for subsequent post-test analyses.

10.5 Operating Conditions for Loop 1 and 2 Through Operations Cycle 2.

Operating temperatures, pressures, and flowrates for lead Test 1 (Loop 1) measured during the HFT cycle and Operations cycles 1 and 2 are presented as monthly tabulations in Tables 10-1 through 10-6. Plots of the corresponding temperature and pressure data for the months of November, 1982 through May, 1983 are presented in Figures 10-2 through 10-8. The analogous data for Test 2 (Loop 2) are presented in Tables 10-7 through 10-13 and Figures 10-9 through 10-15, respectively.

The horizontal scale represent a depth below the surface, based on a known sputtering rate of 50 Å/min (Reference 14).

For each curve in Figure 10-16, the fractional area of a 10 nm slice was compared with the total area under the curve. The total area under the curve represents a known quantity of sulfur and the fractional areas are proportional to the fraction of sulfur atoms stopped within each slice. Table 10-14 summarizes the results of the calculation.

The concentration of S in each slice is calculated from the formula

$$x_s = 2f\phi t / (N + 2f\phi t) \quad (10.4-2)$$

where ϕt = ion fluence (ions/cm²) or total dose

f = fraction of ions stopped within the selected slice (Table 1)

N = number of non-sulfur atoms within the slice (estimated at 9×10^{16} atoms, based on pure nickel)

By plotting normalized peak-to-peak heights (Equation 10.4-1) vs. sulfur concentrations (Equation 10.4-2), a calibration curve for sulfur analysis is obtained (Figure 10-17). The calibration curve of Figure 10-17 is based on the data obtained from the standards with 5×10^{15} and 1×10^{16} ions/cm². The data for the third standard need to be corrected for sulfur loss due to sputtering during ion implantation, an effect that can be neglected for the lower fluences.

Determination of Detection Limits

When the sulfur peak-to-peak height becomes less than twice the noise level in the derivative Auger spectrum, the apparent sulfur concentration may be 100 percent in error and that concentration constitutes the instrumental detection limit. Lower concentrations will go undetected or will be determined with very low accuracy if detected. The instrumental detection limit for this investigation is encountered at the last point of each of the curves in Figure 10-16. From Table 10-14, the corresponding number of S atoms is calculated to be $0.006 \times 5 \times 10^{15} \times 2 = 6 \times 10^{13}$ atoms in a 10 nm slice.

This is converted to $\mu\text{g}/\text{cm}^2$ by multiplying the number of atoms by the mass of a sulfur atom (1.66×10^{-27} kg \times 32). The result is a detection limit of 3×10^{-3} $\mu\text{g}/\text{cm}^2$ in a 10 nm slice.

Analysis of Conditioned Samples

Six areas were analyzed on Inconel 600 samples cut from TMI-1 OTSG tubes which had been subjected to elevated temperature conditioning in simulated reactor coolant chemistry. No sulfur was detected in any of the specimens at any depth level, but all areas showed significant boron levels. The boron signal in the Auger spectrum consisted of two peaks, the main peak at 170 eV and a secondary peak at 152 eV. The peak-to-peak height of the secondary peak was about half that of the main peak. Normal boron signals consist of only one peak at 179 eV. The reason for the shift and the appearance of a second peak is not clear at this time. One possibility is that a boron-compound was formed, but the compound has not been identified.

Because of the proximity of the second boron peak and the sulfur signal, X-ray photoelectron spectroscopy (XPS) was used to differentiate between sulfur and boron. The XPS boron signal consisted of a single line indicating a 1s binding energy of 190.9 eV. No sulfur was detected by XPS. This limits the amount of sulfur that might have been present to $0.15 \mu\text{g}/\text{cm}^2$ in the first 100 nm below the surface and to one tenth of that amount within the first 10 nm below the surface.

The Auger analyses are summarized in "composition tables" attached to the report. The compositions given are essentially normalized peak-to-peak heights (similar to Equation 10.4-1, for each element) and not calibrated. They give, however, some qualitative idea of how the composition changes with sputtering time. The sputter rate used was 5 nm/min.

Summary

Calibration curves for AES analysis of sulfur in Inconel 600 are available. Unfortunately, the presence of an unidentified boron compound makes the use of AES on the GPU-N tubes undesirable, at least for sulfur analysis. XPS is less

sensitive to sulfur, but can be used to differentiate between boron and sulfur. The detection limit for sulfur (by XPS) has been determined. Standards are available to calibrate the XPS technique for quantitative sulfur analysis. (However, the calibration is costly and time consuming.)

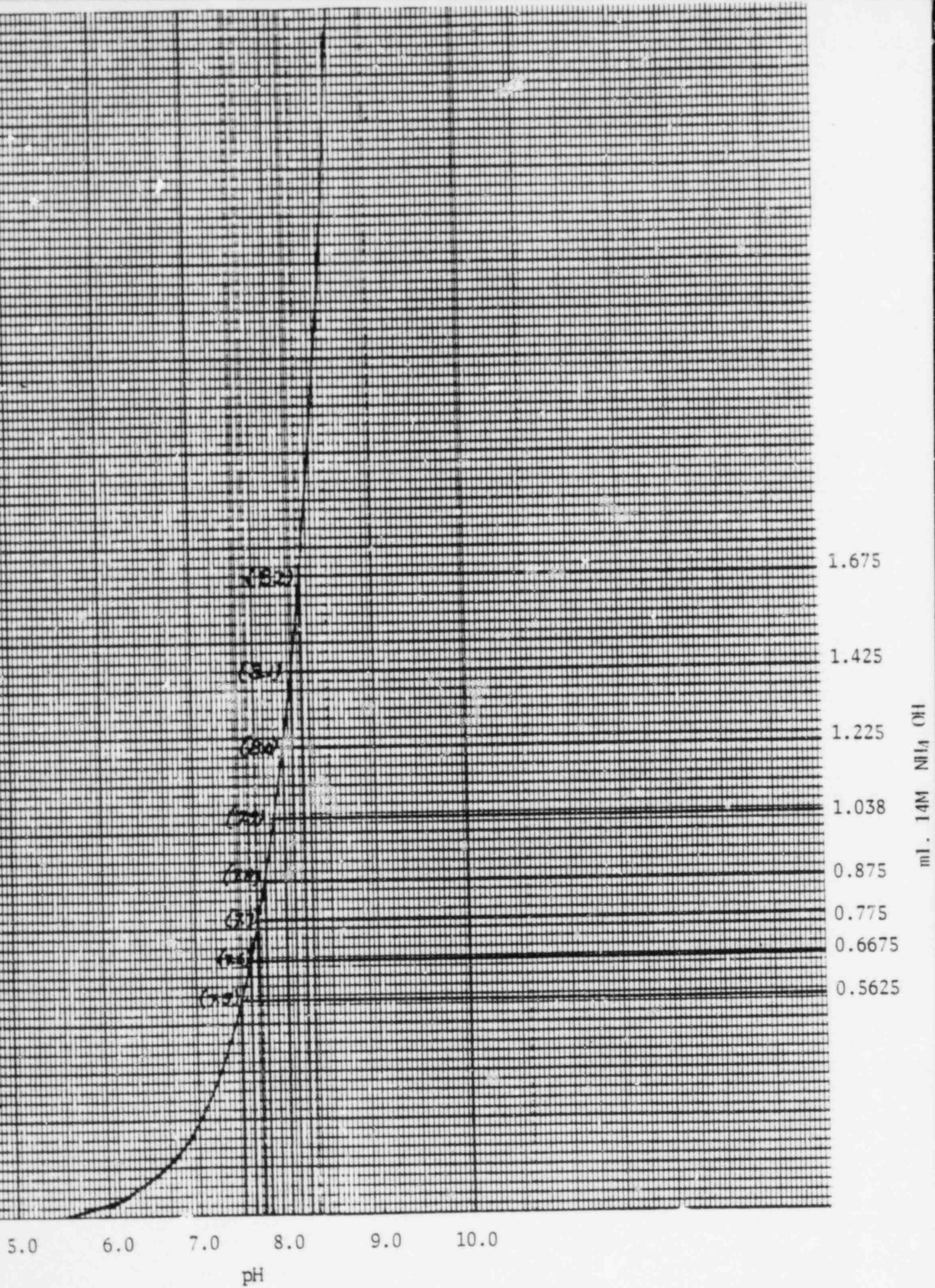


FIGURE 10-1 TITRATION CURVE

AUTOCLAVE #31 NOVEMBER 1982

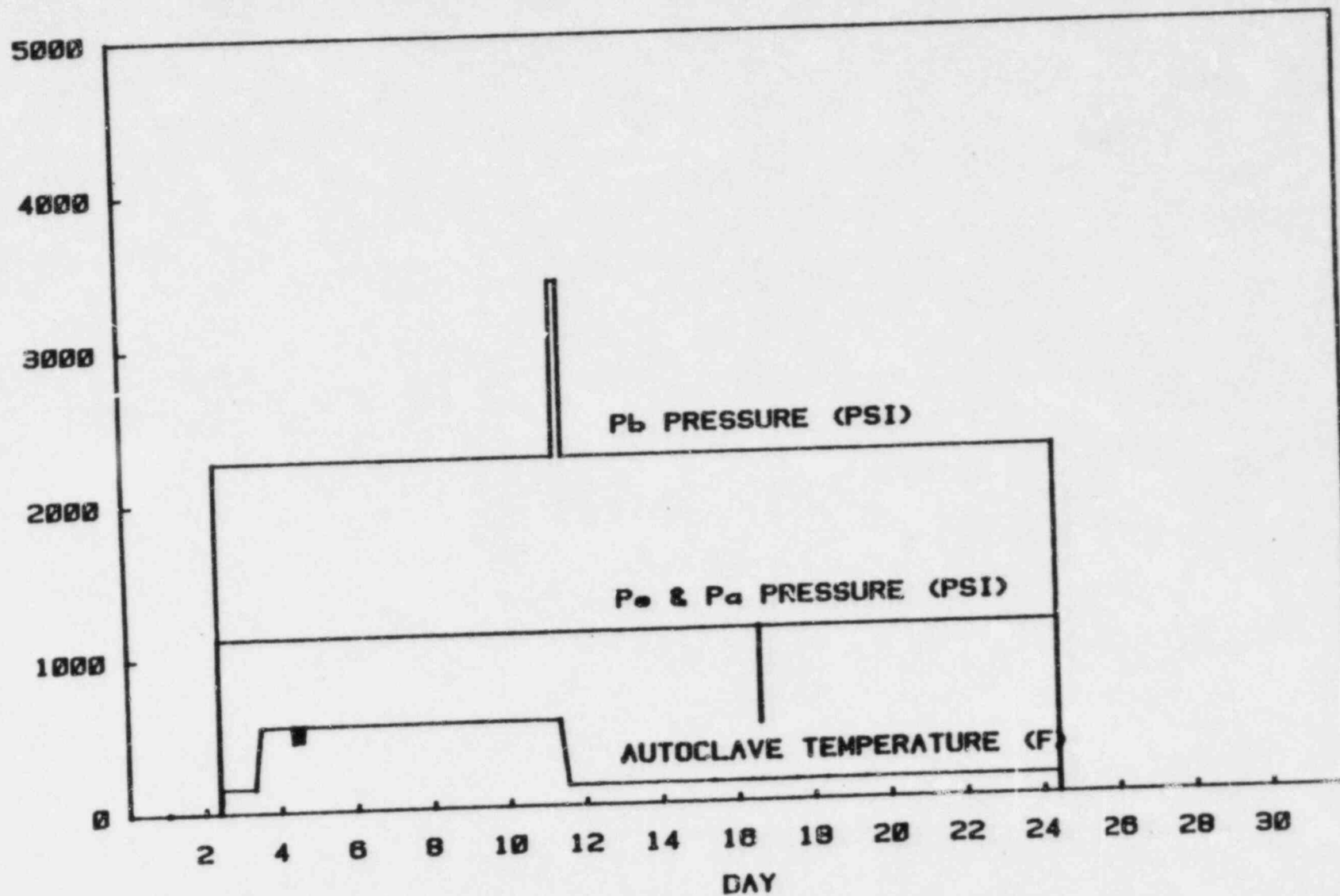


FIGURE 10-2 NOVEMBER OPERATING CONDITIONS FOR TEST 1

AUTOCLAVE #31 DECEMBER 1982

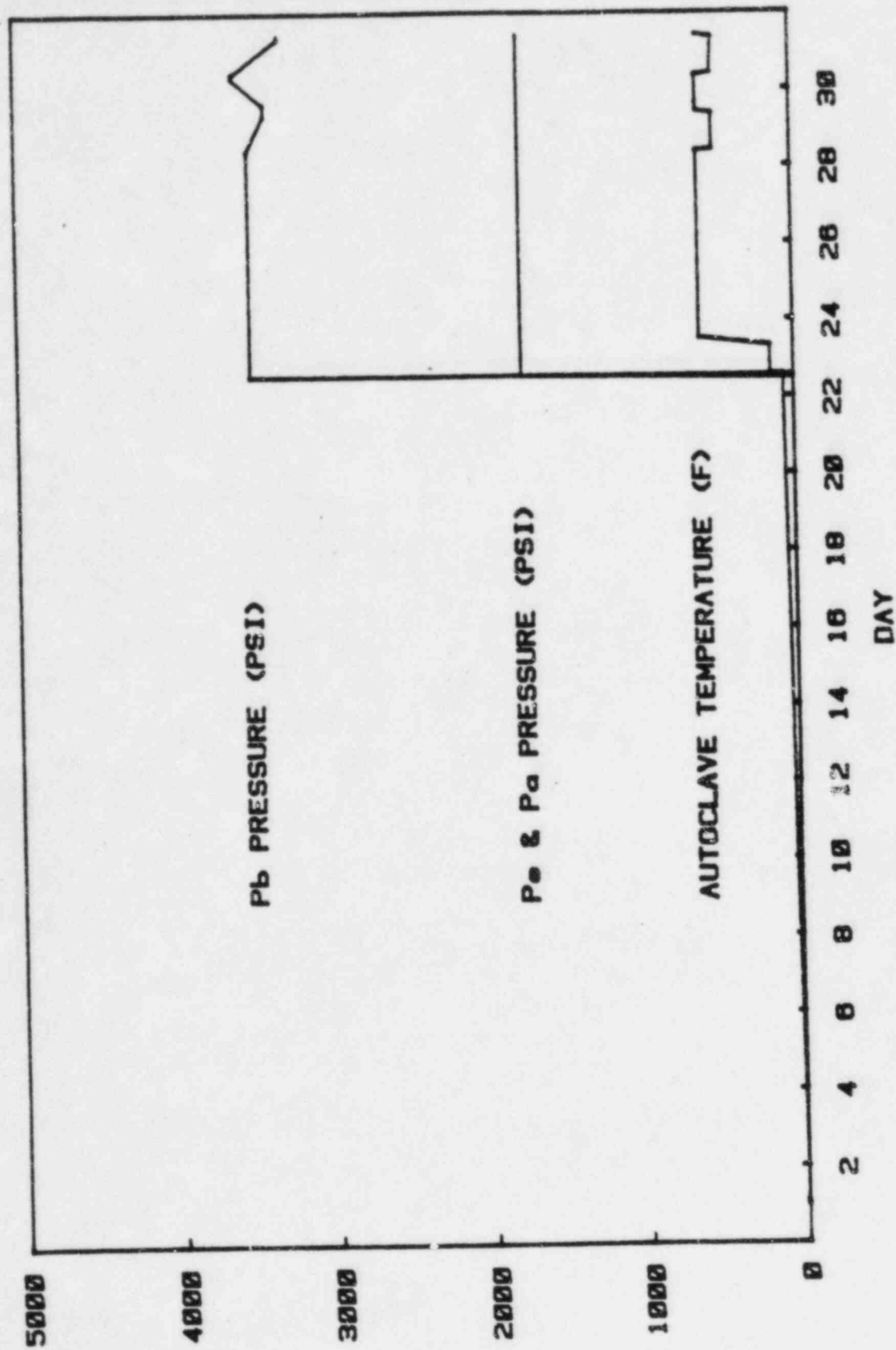


FIGURE 10-3 DECEMBER OPERATING CONDITIONS FOR TEST 1

AUTOClave #31 JANUARY 1983

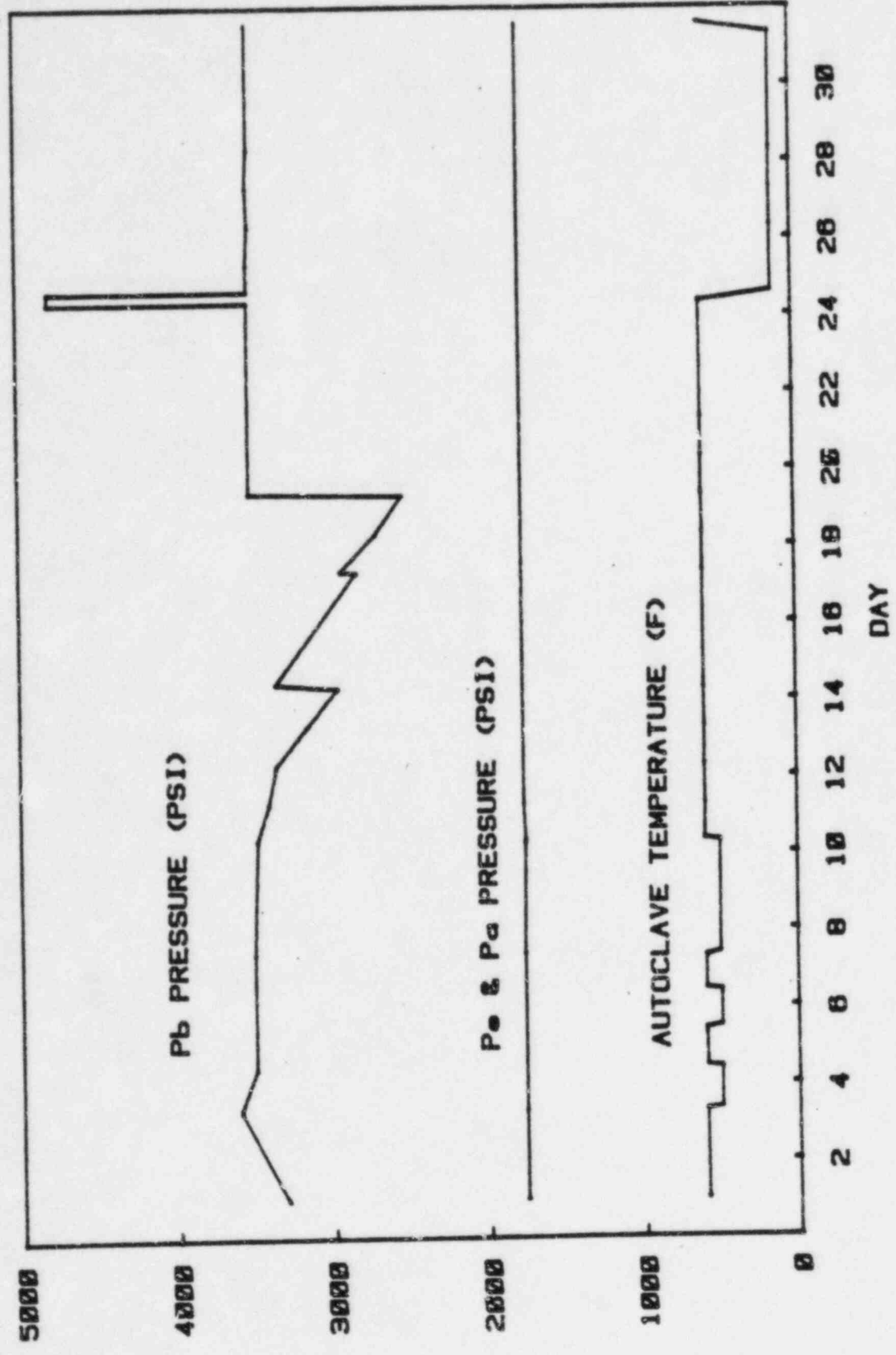


FIGURE 10-4 JANUARY OPERATING CONDITIONS FOR TEST 1.

AUTOCLAVE #31 MONTH OF FEBRUARY

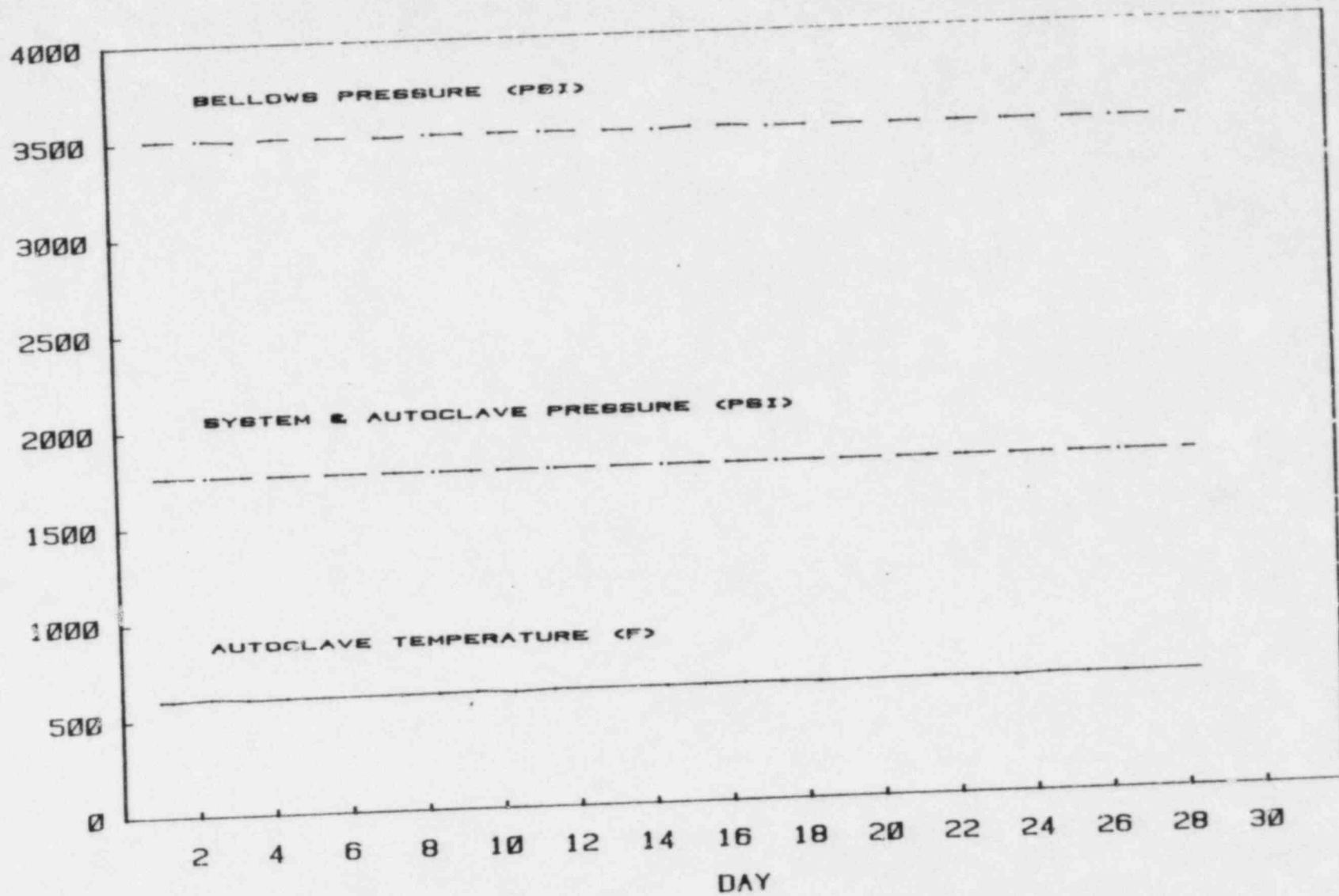


FIGURE 10-5 FEBRUARY OPERATING CONDITIONS FOR TEST 1

AUTOCLAVE #31 MONTH OF MARCH

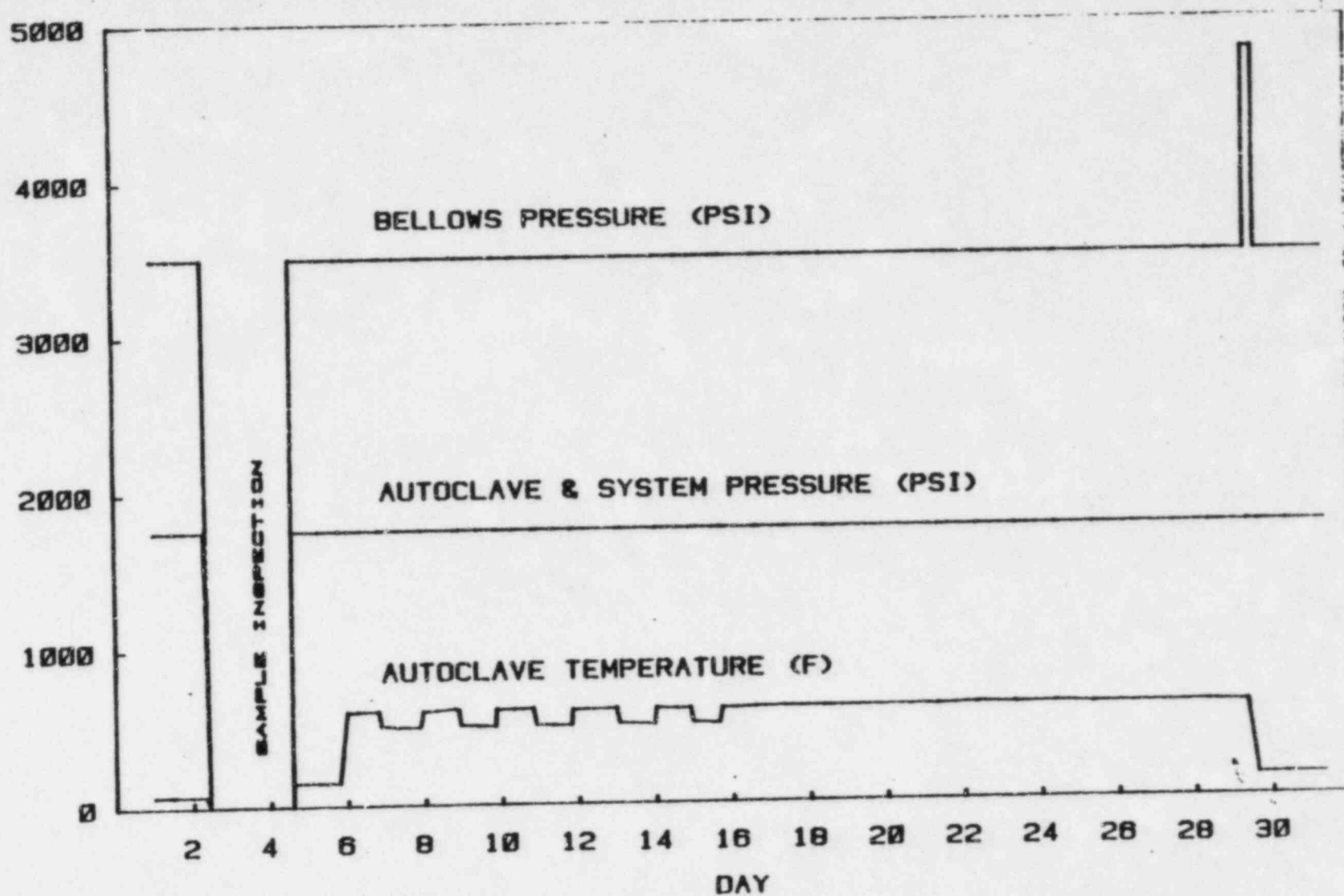


FIGURE 10-6 MARCH OPERATING CONDITIONS FOR TEST 1

AUTOCLAVE #31 MONTH OF APRIL

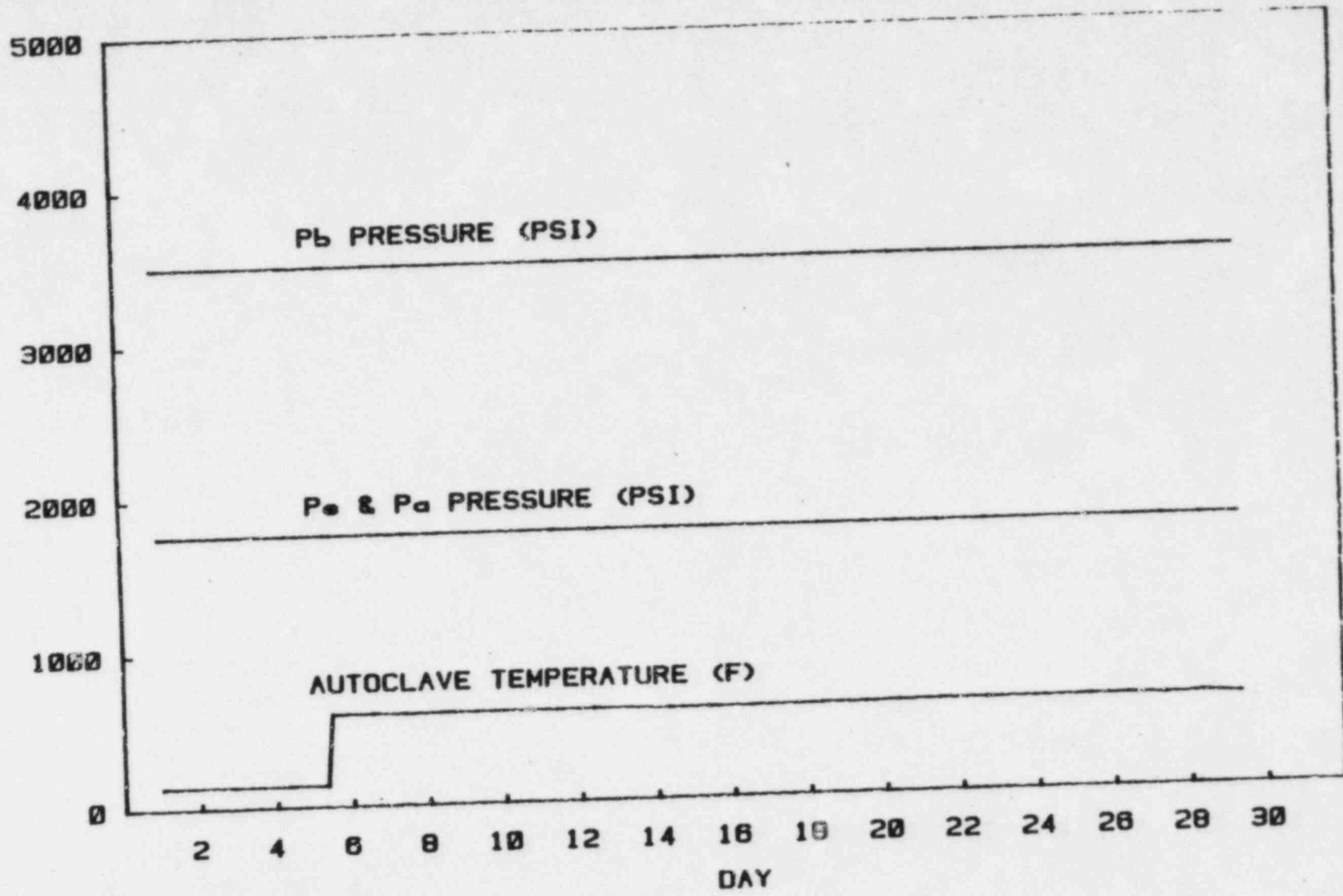


FIGURE 10-7 APRIL OPERATING CONDITIONS FOR TEST 1

AUTOCLAVE #31 MONTH OF MAY

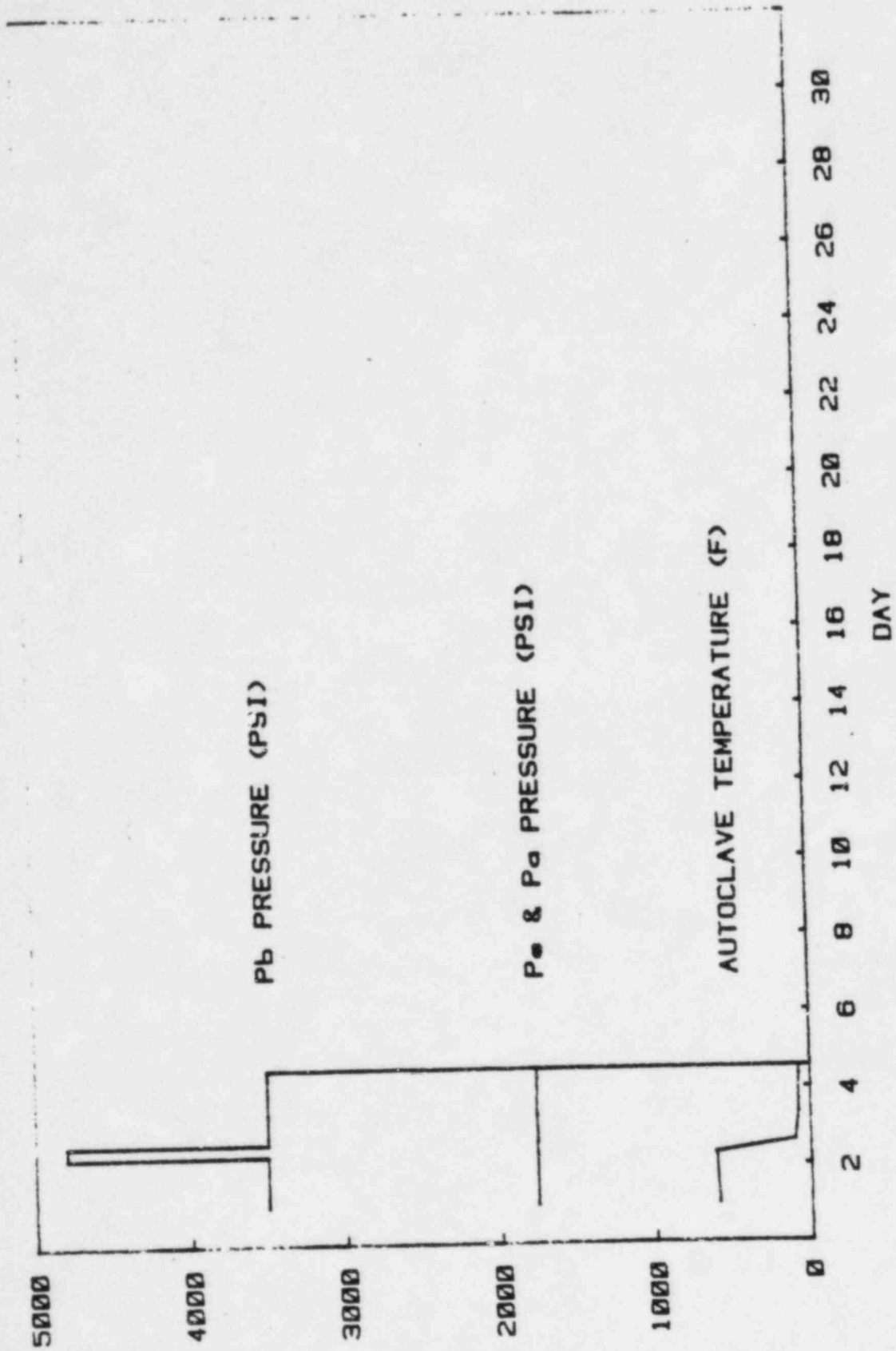


FIGURE 10-8 MAY OPERATING CONDITIONS FOR TEST I

AUTOClave #29 OCTOBER 1982

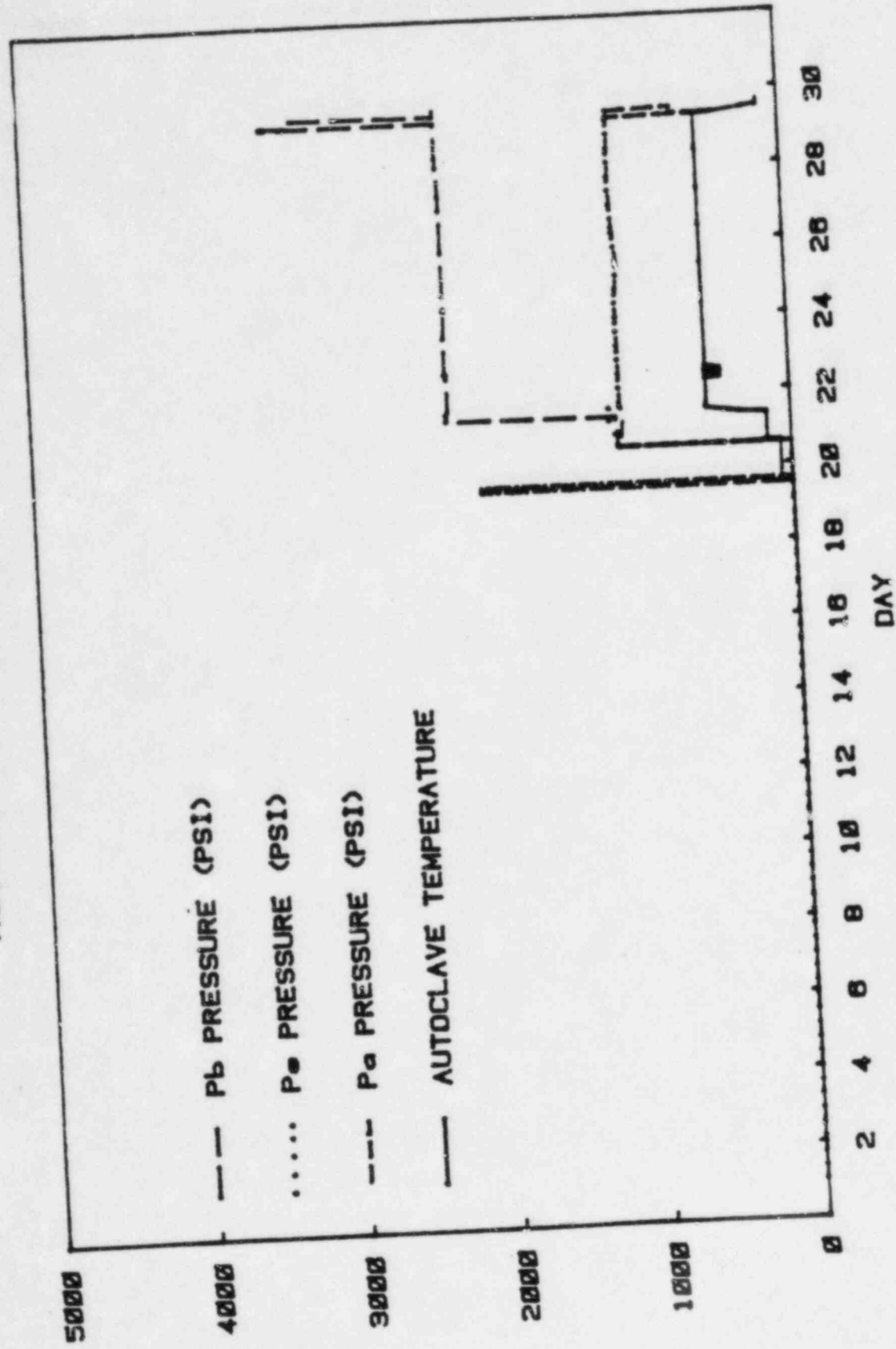


FIGURE 10-9 OCTOBER OPERATING CONDITIONS FOR TEST 2

AUTOCLAVE #29 NOVEMBER 1982

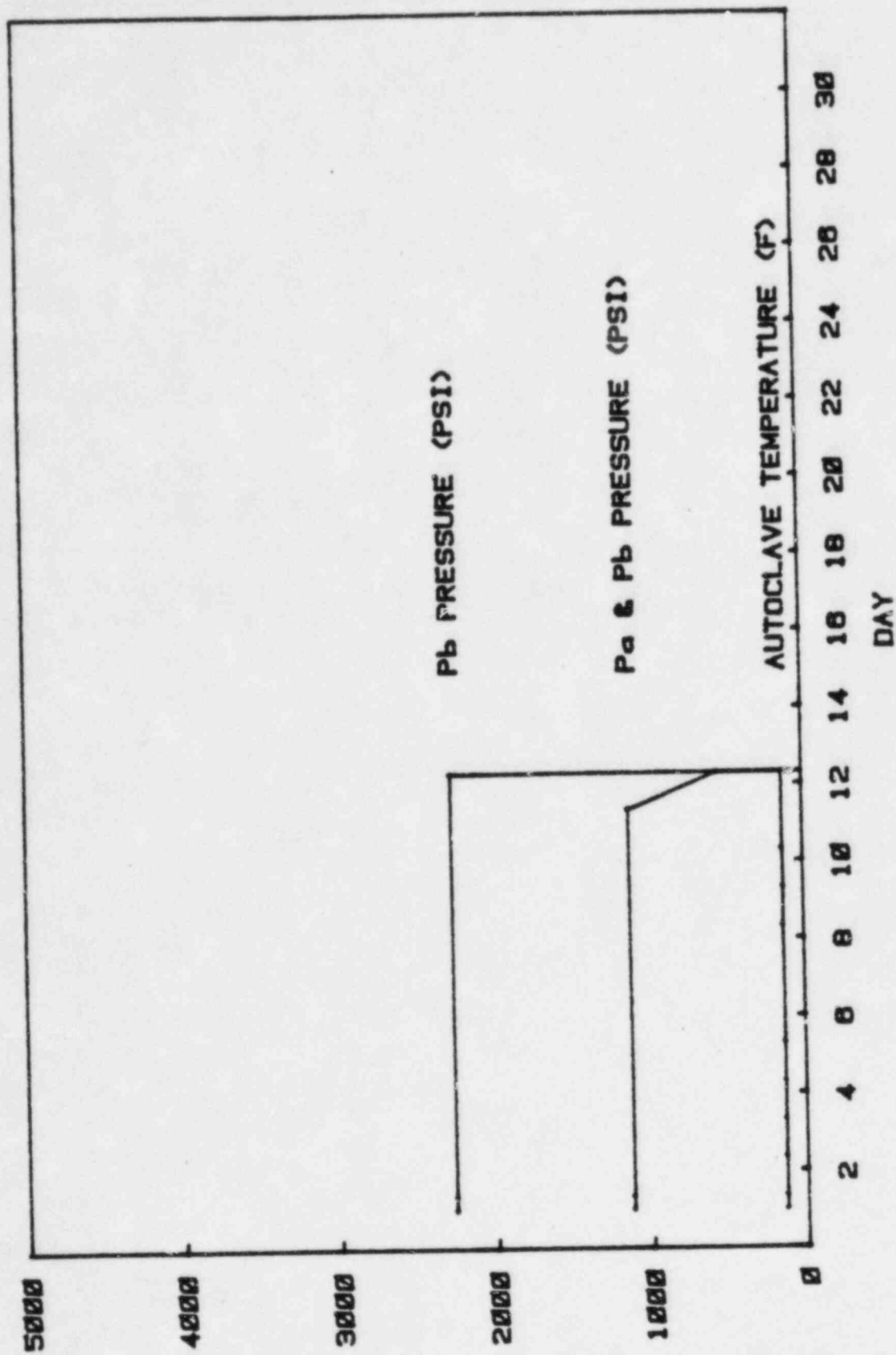


FIGURE 10-10 NUMBER OPERATING CONDITIONS FOR TEST 2

AUTOClave #28 DECEMBER 1982

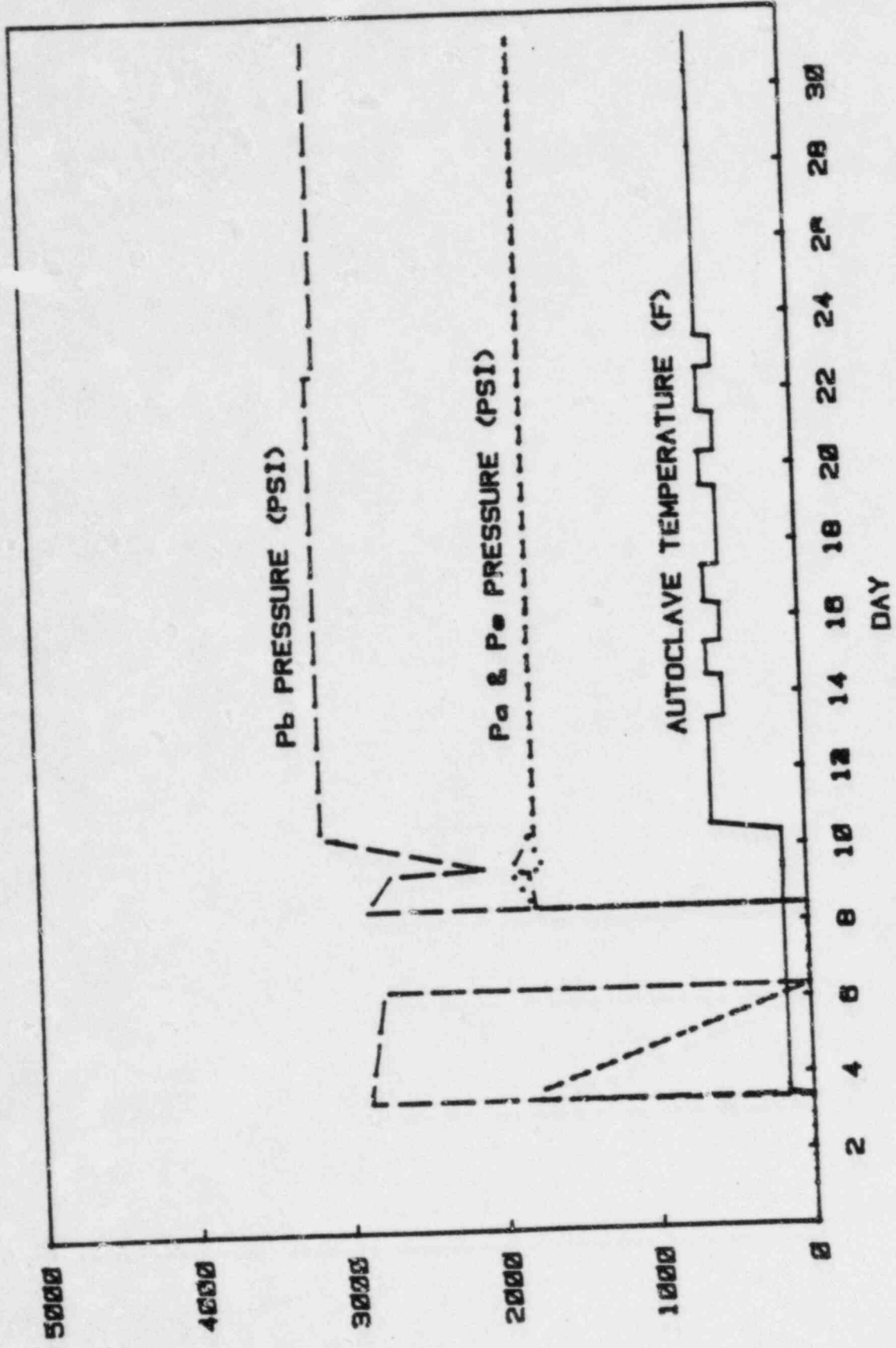


FIGURE 10-11 DECEMBER OPERATING CONDITIONS FOR TEST 2

AUTOCLAVE #29 JANUARY 1983

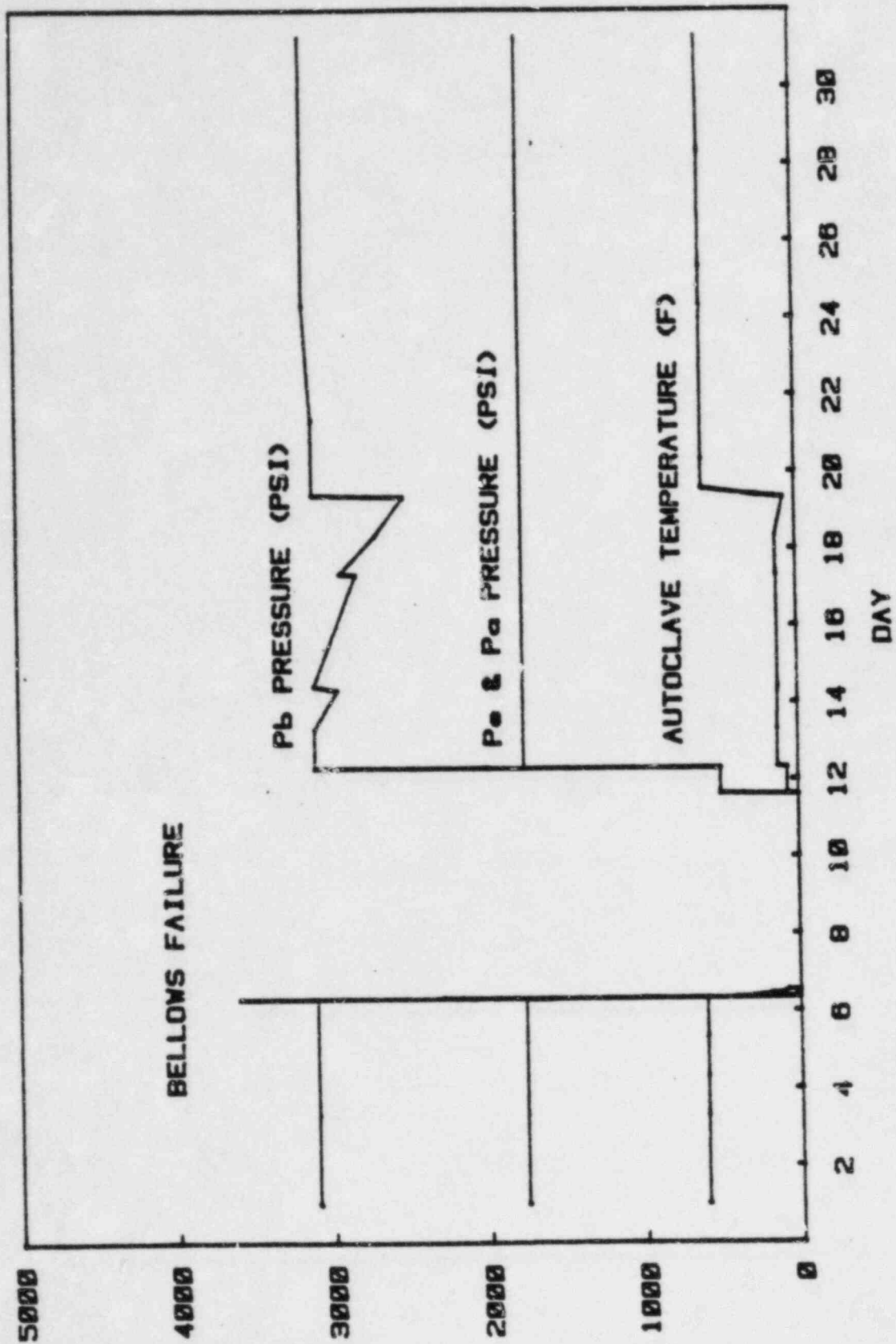


FIGURE 10-12 JANUARY OPERATING CONDITIONS FOR TEST 2

AUTOCLAVE #29 MONTH OF FEBRUARY

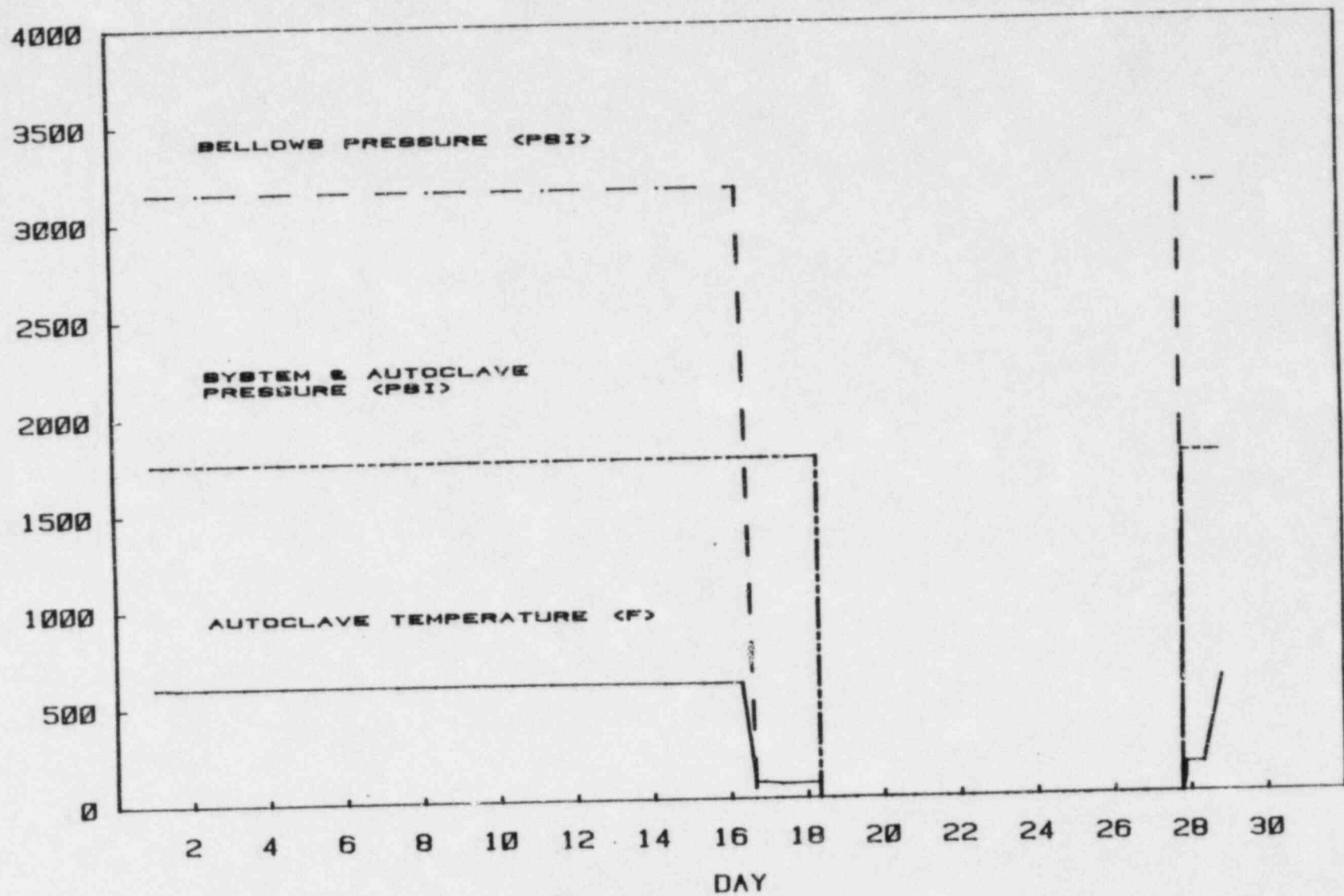


FIGURE 10-13 FEBRUARY OPERATING CONDITIONS FOR TEST 2

AUTOCLAVE #29 MONTH OF MARCH

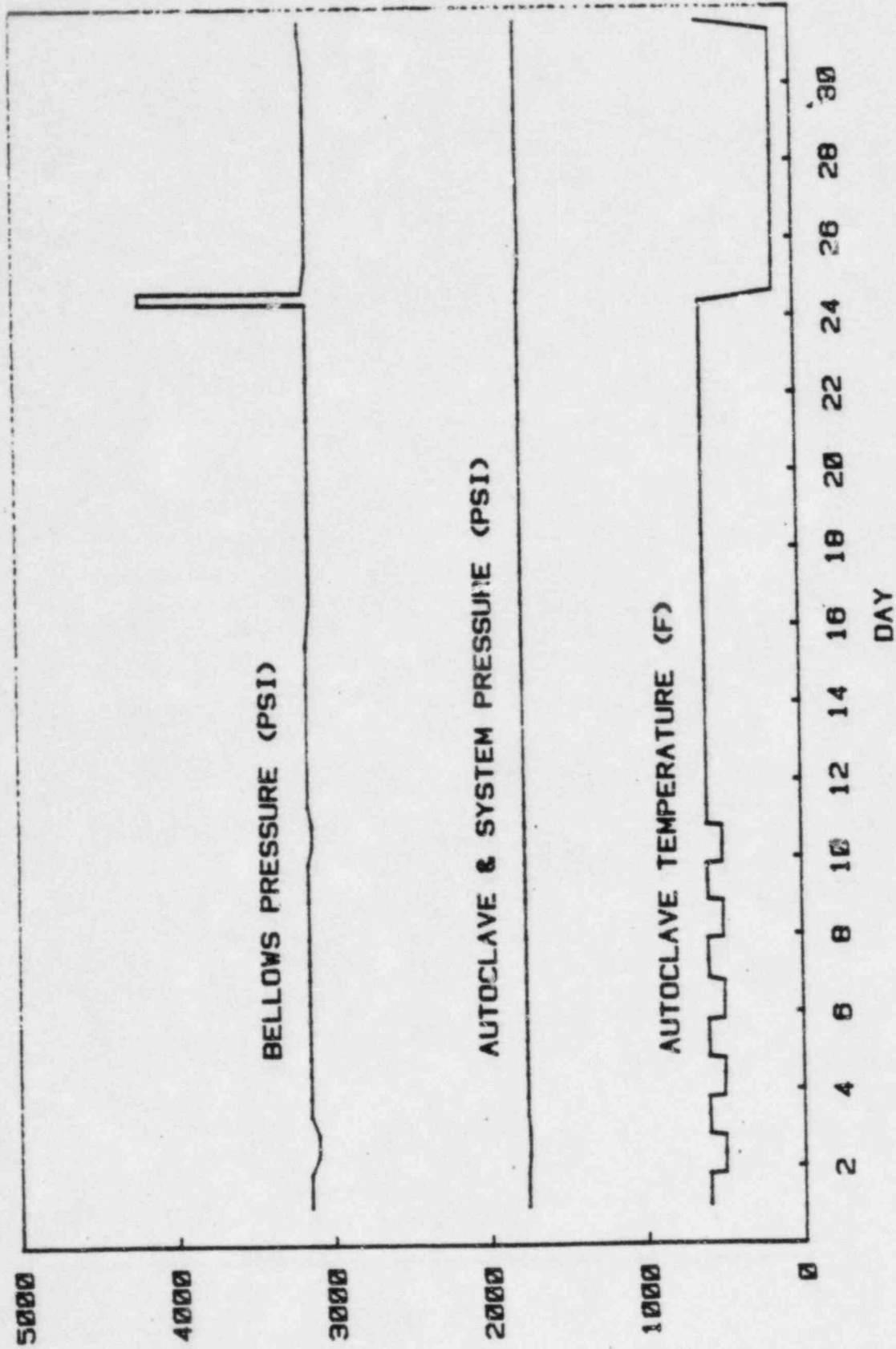


FIGURE 10-14 MARCH OPERATING CONDITIONS FOR TEST 2

AUTOClave #29 MONTH OF APRIL

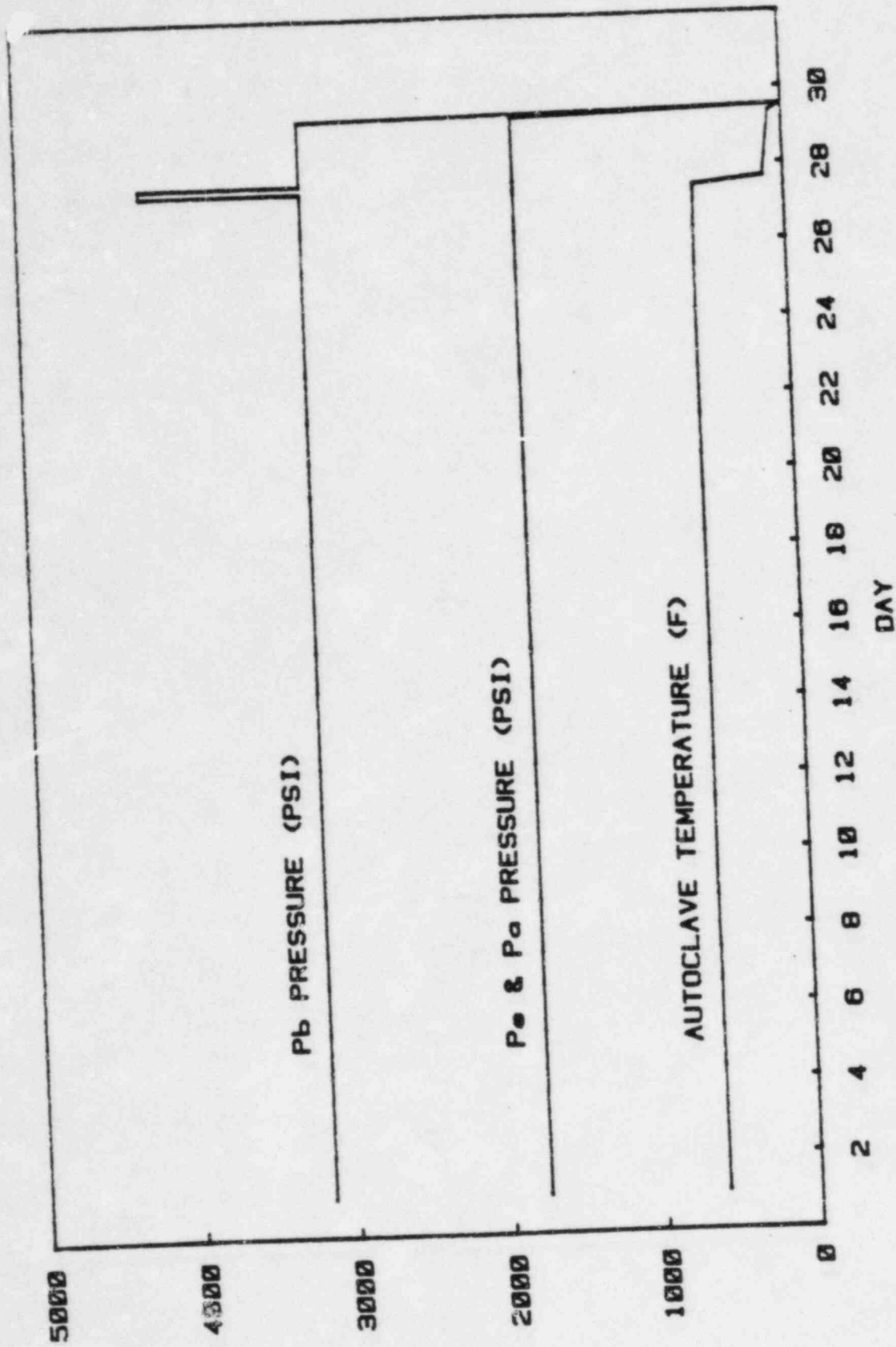


FIGURE 10-15 APRIL OPERATING CONDITIONS FOR TEST 2

TABLE 10-1

OPERATING PARAMETERS FOR TEST LOOP 1

JTOCLAVE#31 TMI LEAD TEST #1
 JUEMBER 1982

AY	TIME	P _s PSI	P _a PSI	P _b PSI	P _{mut} PSI	AC T F	MUT T F	MUT LEVEL INCHES	EFFLUENT F ml/hr
2	905	0	0	0	12	69	69	21.4 *	53
2	955	1120	1120	0	12	69	69		
2	1003	1120	1120	2260	12	69	69		
2	1029	1120	1120	2260	12	155	70	21.3	53
3	740	1120	1120	2260	13	153	73	20.3	51
3	745	1120	1120	2260	13	153	73		
3	1200	1120	1120	2260	13	545	73		
3	1400	1120	1120	2260	13	545	73		
4	744	1120	1120	2260	13	549	74	19.0	85
4	845	1120	1120	2260	13	445	74		
4	945	1120	1120	2260	13	550	74		
4	1030	1120	1120	2260	13	448	74		
4	1130	1120	1120	2260	13	550	74		
4	1230	1120	1120	2260	13	453	74		
4	1330	1120	1120	2260	13	548	74		
4	1430	1120	1120	2260	13	450	74		
4	1525	1120	1120	2260	13	550	74		
5	727	1120	1120	2260	13	548	72	17.8 *	93
3	734	1120	1120	2260	13	549	71	14.3	86 *
7	733	1120	1120	2260	13	550	72	13.1	96
0	734	1120	1120	2260	13	550	71	12.0	101 *
1	728	1120	1120	2260	13	550	72	10.8	94
1	800	1120	1120	3400	13	550	72		
1	1300	1120	1120	3400	13	132	72		
1	1305	1120	1120	2260	13	132	72		
1	1515	1120	1120	2260	0	131	70	10.0	101
2	738	1120	1120	2260	0	132	70	9.1 *	105
5	725	1120	1120	2260	0	131	74	28.8	98
6	720	1120	1120	2260	0	130	73	27.5	102
6	1420	1120	1120	2260	0	130	73		
6	1420	500	500	2260	0	130	73		
6	1421	1120	1120	2260	0	130	73		
7	1120	1120	1120	2260	0	131	73	36.3	98
8	738	1120	1120	2260	0	132	72	24.9	99
9	735	1120	1120	2260	0	131	72	23.8	102
2	720	1120	1120	2260	0	130	72	19.8	98
3	735	1120	1120	2260	0	130	72	18.6	97 *
4	725	1120	1120	2260	0	130	72	17.3	98
4	950	1120	1120	2260	0	130	72		
4	955	0	0	0	0	0	72		

OTE ** INDICATES MUT OR EFFLUENT SAMPLE TAKEN

COMMENTS:

AY

MUT SAMPLE PH-5.6 CONDUCTIVITY 68 UOHM

1 MUT OPENED TO ATMOSPHERE

2 MUT REFILL

TABLE 10-2

OPERATING PARAMETERS FOR TEST LOOP 1

TOCLAVE#31 TMI LEAD TEST #1
 DECEMBER 1982

Y	TIME	P _s PSI	P _a PSI	P _b PSI	P _{mut} PSI	AC T F	MUT T F	MUT LEVEL INCHES	EFFLUENT F ml/hr
	1125	0	0	0	15	66	66	20.5 *	72
	1330	1760	1760	0	15	66	69		
	1332	1760	1760	3510	15	66	69		
	1335	1760	1760	3510	15	68	69		
	1422	1760	1760	3510	15	148	69		
	745	1760	1760	3510	15	149	73	19.8	62
	750	1760	1760	3510	15	149	73		
	1258	1760	1760	3510	15	600	73		
	840	1760	1760	3510	15	603	75	15.3	77
	905	1760	1760	3510	15	603	75		
	1005	1760	1760	3510	15	499	75		
	820	1760	1760	3400	15	500	72	14.1	64
	835	1760	1760	3400	15	500	72		
	1020	1760	1760	3400	15	600	72		
	1515	1760	1760	3400	15	600	72		
	800	1760	1760	3600	15	602	82	13.0	64
	830	1760	1760	3600	15	602	82		
	1000	1760	1760	3600	15	502	82		
	820	1760	1760	3300	15	495	84	11.9	98
	835	1760	1760	3300	15	495	84		
	1020	1760	1760	3300	15	596	84		

TE "*" INDICATES MUT OR EFFLUENT SAMPLE TAKEN

TABLE 10-3
OPERATING PARAMETERS FOR TEST LOOP 1

CLAVE#31 TMI LEAD TEST #1
ARY 1985

TIME	P _s PSI	P _a PSI	P _b PSI	F _{mut} PSI	AC T F	MUT T F	MUT LEVEL INCHES	EFFLUENT F ₁ ml/hr
735	1760	1760	3600	15	601	82	8.8	120
740	1760	1760	3600	15	601	82		
925	1760	1760	3600	15	503	82	7.5	92
1014	1760	1760	3500	15	502	81		
1015	1760	1760	3500	15	502	81	31.0 *	92
1150	1760	1760	3500	15	597	81		
740	1760	1760	3500	15	602	80		
1020	1760	1760	3500	15	602	80		
1220	1760	1760	3500	15	501	80	20.8	78
725	1760	1760	3500	15	500	81		
1010	1760	1760	3500	15	500	81		
1140	1760	1760	3500	15	599	81	27.5	62
720	1760	1760	3500	15	597	78		
735	1760	1760	3500	15	597	78		
1005	1760	1760	3500	15	505	78	24.0	110
735	1750	1750	3475	15	501	79		
740	1750	1750	3475	15	501	79		
900	1750	1750	3475	15	600	79	22.9	89
735	1760	1760	3400	15	597	79	21.6	96
745	1760	1760	3350	15	600	79	20.5	115
745	1760	1760	3150	15	598	79	19.5	120
747	1760	1760	2950	15	600	79		
1040	1760	1760	3350	15	600	79	15.8	97
745	1760	1760	2825	15	600	79		
810	1760	1760	2925	15	600	79	15.6	99
740	1760	1760	2700	15	598	77	13.5	94
748	1760	1760	2525	15	602	79		
915	1760	1760	3510	15	602	79	12.3	116
750	1760	1760	3510	15	599	76	11.3	115
755	1760	1760	3510	15	598	78	7.8	86
745	1760	1760	3510	15	599	78		
810	1760	1760	3510	15	599	78		
810	1760	1760	4795	15	599	78		
1450	1760	1760	4795	15	131	78		
1510	1760	1760	4795	15	131	78		
1510	1760	1760	3510	15	131	73	7.0	79
1545	1760	1760	3510	15	131	71	6.5	91 *
732	1760	1760	3510	15	131	70	5.0 *	95
730	1760	1760	3500	15	131	70	36.3	90
735	1760	1760	3510	15	133	70	25.3	90
745	1760	1760	3500	15	133	72	22.0	91
730	1760	1760	3500	15	131	73		
740	1760	1760	3500	15	131	73		
1400	1760	1760	3500	15	596	73		

NOTE ** INDICATES MUT OR EFFLUENT SAMPLE TAKEN

COMMENTS:

AY

MUT REFILL (50L)

- BELLOWS NITROGEN SUPPLY LOW
- BELLOWS NITROGEN SUPPLY RESTORED

OPERATING PARAMETERS FOR TEST LOOP 1

AUTOCLAVE#31 TMI LEAD TEST #1
FEBRUARY 1983

DAY	TIME	Ps PSI	Pa PSI	Pb PSI	Pmut PSI	AC T F	MUT T F	MUT LEVEL INCHES	EFFLUENT FLOW ml/hr
1	735	1760	1760	3510	15	598	77	21.0	104 *
2	800	1760	1760	3510	15	605	78	17.9	101
3	745	1760	1760	3500	15	597	80	18.5	79
4	808	1760	1760	3510	15	599	78	17.5	117
7	745	1760	1760	3500	15	600	79	14.5	108
8	735	1760	1760	3510	15	601	84	13.5	128 *
9	745	1760	1760	3510	15	604	84	12.3	134 *
10	735	1760	1760	3510	15	596	84	11.3	99
11	805	1760	1760	3510	15	604	84	10.1 *	75
14	747	1760	1760	3500	15	603	81	27.3	88
15	734	1760	1760	3510	15	603	82	26.3	92
16	805	1760	1760	3510	15	605	80	25.1	93
17	745	1760	1760	3500	15	602	78	24.0	92
18	730	1760	1760	3500	15	597	77	23.0	80
21	740	1760	1760	3500	15	602	76	19.6	106
22	735	1760	1760	3500	15	601	73	18.5	100
23	1107	1760	1760	3500	15	595	77	17.4	94 *
24	753	1760	1760	3500	15	604	81	16.5	87
25	815	1760	1760	3500	15	602	78	15.6	92
26	745	1760	1760	3500	15	601	79	14.3	88
28	740	1760	1760	3500	15	604	80	12.0	80

NOTE ** INDICATES MUT OR EFFLUENT SAMPLE TAKEN

COMMENTS:

DAY

11 REFILL MUT (11:10) 02 < 5 PPB. COND. = 53 uOHM PH=6.03

OPERATING PARAMETERS FOR TEST LOOP 1

TOCLAVE#31 TMI LEAD TEST #1
RCH 1983

TIME	P _s PSI	P _a PSI	P _b PSI	P _{mut} PSI	AC T F	MUT T F	MUT LEVEL INCHES	EFFLUENT ml/hr
1005	1760	1760	3500	8	72	73	9.5	65
740	1760	1760	3500	8	72	71	8.1	68 *
1030	0	0	0	0	0	0	0.0	0
1400	0	0	0	0	0	0		
1430	1760	1760	3500	15	152	73	23.8 *	115 *
640	1760	1760	3500	15	151	76	23.0	65
1900	1760	1760	3500	15	150	76		
2400	1760	1760	3500	15	590	76		
630	1760	1760	3500	15	599	77	22.0	85
1910	1760	1760	3500	15	600	77		
2110	1760	1760	3500	15	504	77		
735	1760	1760	3500	15	497	79	21.0	72
2110	1760	1760	3500	15	495	79		
2310	1760	1760	3500	15	596	79		
1850	1760	1760	3500	15	611	78	19.5	127
2100	1760	1760	3500	15	602	78		
2230	1760	1760	3500	15	505	78		
915	1760	1760	3500	15	500	78	18.8	96 *
2000	1760	1760	3500	15	495	78		
2100	1760	1760	3500	15	604	78		
740	1760	1760	3500	15	606	81	17.3	97
1940	1760	1760	3500	15	610	81		
2155	1760	1760	3500	15	503	81		
830	1760	1760	3500	15	498	79	17.0	96
1930	1760	1760	3500	15	498	79		
2030	1760	1760	3500	15	598	79		
2330	1760	1760	3500	15	604	79		
135	1760	1760	3500	15	505	79		
2310	1760	1760	3500	15	497	79		
25	1760	1760	3500	15	601	79		
1300	1760	1760	3500	15	596	79	13.5	84
2115	1760	1760	3500	15	600	79		
2315	1760	1760	3500	15	504	79		
1150	1760	1760	3500	15	499	78	11.8	87
1545	1760	1760	3500	15	500	78		
1715	1760	1760	3500	15	595	78		
1320	1760	1760	3500	15	603	78	10.5	70
810	1760	1760	3500	15	604	79	9.8	74
810	1760	1760	3500	15	603	84	8.8	72
745	1760	1760	3500	15	603	80	5.5 *	125
740	1760	1760	3500	15	610	81	27.9	125
750	1760	1760	3500	15	605	83	26.8	116 *
800	1760	1760	3500	15	609	80	25.5	91
810	1760	1760	3500	15	602	82	24.5	150
800	1760	1760	3500	15	604	84	22.0	40
750	1760	1760	3500	15	598	81	21.5	41
814	1760	1760	3500	15	598	81		
815	1760	1760	4795	15	598	81		
1435	1760	1760	4795	15	135	81		
1440	1760	1760	3500	15	135	81		
800	1760	1760	3500	15	136	77	19.5	108
810	1760	1760	3500	15	134	76	18.5	108

TE ** INDICATES MUT OR EFFLUENT SAMPLE TAKEN

OPERATING PARAMETERS FOR TEST LOOP 1

JTOCLAVE#31 TMI LEAD TEST #1
 APRIL 1983

AY	TIME	Ps PSI	Pa PSI	Pb PSI	Pmut PSI	ACT F	MUT F	MUT LEVEL INCHES	EFFLUENT F ml/hr
1	750	1760	1760	3500	15	135	78	3.0	112
1		1710	1760	3500	15	135	78	11.5	110
3	805	1760	1760	3500	15	134	78		
5	1150	1760	1760		15	597	78		
5	1300	1760	1760	3500	15	598	77	10.3	120 *
7	905	1760	1760	3500	15	594	75	9.0	102
3	815	1760	1760	3500	15	597	75	7.0 *	107
1	805	1760	1760	3500	15	595	76	27.8	104
2	745	1760	1760	3500	15	599	75	26.8	110
4	800	1760	1760	3500	15	588	76	24.9	120
5	850	1760	1760	3500	15	589		23.5	124
3	755	1760	1760	3500	15	593	75	19.8	94
9	1120	1760	1760	3500	15	593	73	18.3	105
0	805	1760	1760	3500	15	597	71	17.3	101 *
1	1005	1760	1760	3500	15	599	71	16.0	95
2	1525	1760	1760	3500	15	597	76	14.5	97
5	827	1760	1760	3500	15	602	77	11.3	192
5	805	1760	1760	3500	15	603	76	9.8	180
7	750	1760	1760	3500	15	596	80	8.4	191
3	755	1760	1760	3500	15	604	88	7.5	93
9	800	1760	1760	3500	15	591	77	6.5	136

NOTE: ** INDICATES MUT OR EFFLUENT SAMPLE TAKEN

COMMENTS:

AY
 REFILLED MUT
 AY 1983

AY	TIME	Ps PSI	Pa PSI	Pb PSI	Pmut PSI	ACT F	MUT T F	MUT LEVEL INCHES	EFFLUENT F ml/hr
2	740	1760	1760	3500	15	607	77	6.0	75
2	750	1760	1760	4795	15	607	77		
2	1500	1760	1760	4795	6	100	77		
2	1500	1760	1760	3500	15	100	77		
3	800	1760	1760	3500	10	78	74		
4	755	1760	1760	3500	10	75	75		
4	1300	1760	1760	3500	10	75	75		
4	1300	0	0	0	0	0	0	0.0	0
1	800	0	0	0	0	0	0		

NOTE: ** INDICATES MUT OR EFFLUENT SAMPLE TAKEN

COMMENTS:

AY
 MUT N2 SPARGE (15 MIN.) / MUT 5 PSI AIR

TABLE 10-7

OPERATING PARAMETERS FOR TEST LOOP 2

CLAVE#29 TMI LEAD TEST #2
 BER 19B2

TIME	P _s PSI	P _a PSI	P _b PSI	P _{mut} PSI	AC T F	MUT T F	MUT LEVEL INCHES	EFFLUENT FLO ml/hr
1115	0	0	0	19	71	69	23.4	100
1115	2050	2050	0	12	71	69		
1400	2050	2050	0	12	71	69		
1400	0	0	0	12	71	69		
1330	0	0	0	12	73	70	22.9	100
1330	1120	1120	1140	12	73	70		
1418	1120	1120	1140	12	73	70		
1430	1120	1120	1140	12	150	70		
1520	1120	1120	1140	12	155	70		
721	1200	1100	1150	13	154	72	20.6	100
816	1200	1100	1150	13	154	72		
913	1200	1110	2260	13	335	72		
1000	1200	1110	2260	13	400	72		
1200	1200	1110	2260	13	548	72		
1340	1200	1110	2260	13	549	72		
1525	1120	1120	2250	13	547	72		
650	1120	1120	2250	13	548	72		
742	1120	1120	2250	13	553	72		
840	1120	1120	2250	13	545	72		
923	1120	1120	2250	13	450	72		
1023	1120	1120	2250	13	550	72		
1115	1120	1120	2250	13	446	72		
1210	1120	1120	2250	13	552	72		
1300	1120	1120	2250	13	448	72		
1505	1120	1120	2250	13	545	72	20.3	108
1505	1120	1120	2260	12	545	73	18.9	63
740	1120	1120	2250	13	548	72	18.8 *	102 *
811	1100	1100	2250	13	548	72	17.6	90
830	1120	1120	2250	13	547	73	16.5	120
835	1130	1130	2250	13	547	73	15.5 *	93 *
842	1125	1125	2260	13	548	73	14.3	112
728	1120	1120	2260	13	548	73		
730	1120	1120	3400	13	548	73		
820	450	450	3400	13	437	73		
820	700	700	3200	13	437	73		
1055	700	700	3200	13	225	73		
1235	700	700	3200	13	135	73		
1120	1120	1120	2260	13	135	73		
1530	1120	1120	2260	0	133	73		

NOTE: ** INDICATES MUT OR EFFLUENT SAMPLE TAKEN

COMMENTS:

2 15:05 ADDED 75cc OF HALIDE TO MUT

TABLE 10-8
OPERATING PARAMETERS FOR TEST LOOP 2

TOOLAVE#29 TMI LEAD TEST #2
JANUARY 1982

TIME	Ps PSI	Pa PSI	Pb PSI	Pmut PSI	AC T F	MUT T F	MUT LEVEL INCHES	EFFLUENT F ml/hr
835	1120	1120	2260	0	132	67	10.3	91
838	1120	1120	2260	0	132	68	9.0 *	91
742	1120	1120	2260	0	131	70	31.1	113
740	1120	1120	2260	0	131	70	30.6	110
732	1120	1120	2260	0	130	70	29.1 *	128
730	1120	1120	2260	0	131	68	24.9	100
735	1120	1120	2260	0	128	69	23.5	107
732	1120	1120	2260	0	130	69	22.1	94
810	1120	1120	2260	0	130	69	20.8 *	115 *
705	550	550	2260	0	130	69	19.5	0
728	0	0	0	0	0	69		

NOTE: "*" INDICATES MUT OR EFFLUENT SAMPLE TAKEN

REMARKS:

Y
REFILL MUT
PUMP MALFUNCTION

TABLE 10-9
OPERATING PARAMETERS FOR TEST LOOP 2

TIME	INLET PRESSURE (PSI)	OUTLET PRESSURE (PSI)	INLET FLOW (GPM)	OUTLET FLOW (GPM)	ACT F	MUT 1 F	MUT LEVEL INCHES	EFFLUENT ml/l
0	0	0	0	0	0	72	24.0 *	0
15	0	0	0	0	72	72		
30	1750	1750	2850	12	72	72		
45	1750	1750	2850	12	150	72		
1:00	1750	1750	2850	15	151	72	0.0	0
1:15	1750	1750	2850	12	150	72		
1:30	0	0	2750	15	154	72		96
1:45	0	0	0	15	155	72	24.0 *	
2:00	0	0	0	15	155	73		90
2:15	1750	1750	2650	14	148	73	23.0	
2:30	1910	1910	2700	14	148	73		91
2:45	1700	1910	2075	14	148	73	21.5	
3:00	1800	1800	3040	15	151	75		
3:15	1800	1800	3080	15	151	75		
3:30	1750	1750	3150	15	245	75		
3:45	1750	1750	3150	15	600	73	17.3	98
4:00	1750	1750	3150	15	599	74		
4:15	1750	1750	3150	15	599	74		
4:30	1750	1750	3150	15	497	74	16.3	83
4:45	1750	1750	3150	15	501	75		
5:00	1750	1750	3150	15	501	75		
5:15	1750	1750	3150	15	501	75		
5:30	1750	1750	3150	15	598	75	15.5	69
5:45	1750	1750	3150	15	600	75		
6:00	1750	1750	3150	15	600	75		
6:15	1750	1750	3150	15	600	75		
6:30	1750	1750	3150	15	504	73	13.5	110
6:45	1750	1750	3150	15	500	74		
7:00	1750	1750	3150	15	500	74		
7:15	1750	1750	3150	15	598	74		
7:30	1750	1750	3150	15	600	75	12.0	112
7:45	1750	1750	3150	15	600	75		
8:00	1750	1750	3150	15	501	75	8.3	128
8:15	1750	1750	3150	15	502	75		
8:30	1750	1750	3150	15	502	75		
8:45	1750	1750	3150	15	598	75	7.0	100
9:00	1750	1750	3150	15	601	75		
9:15	1750	1750	3150	15	601	75		
9:30	1750	1750	3150	15	504	75	5.5	80
9:45	1750	1750	3150	15	501	74		
10:00	1750	1750	3150	15	501	74		
10:15	1750	1750	3150	15	598	74		
10:30	1750	1750	3150	15	598	74	29.3 *	80
10:45	1750	1750	3150	15	598	74	28.0	95
11:00	1750	1750	3150	15	599	73		
11:15	1750	1750	3150	15	599	73		
11:30	1750	1750	3150	15	512	73		
11:45	1750	1750	3100	15	501	73		
12:00	1750	1750	3100	15	500	74	26.3	109
12:15	1750	1750	3100	15	500	74		
12:30	1750	1750	3100	15	598	74		
12:45	1750	1750	3100	15	598	74		
1:00	1430	1750	1750	15	598	73	19.3	111
1:15	1750	1750	3100	15	598	70	17.9	120
1:30	1750	1750	3100	15	599	80	16.6	96
1:45	1750	1750	3100	15	602	81	15.5	99
2:00	1750	1750	3100	15	602	81		
2:15	1750	1750	3100	15	602	81		

TABLE 10-10
OPERATING PARAMETERS FOR TEST LOOP 2

TEST LOOP TEST #1
DATE: 1/1/70

NO	TIME	PS	PR	PD	Fmut	AC T	MUT T	MUT LEVEL	EFFLUENT
		PSI	PSI	PSI	PSI	F	F	INCHES	ml/hr
3		1760	1760	3100	15	601	80	12.0	78
4		1760	1760	3100	15	600	78	10.6	76
5	800	1760	1760	3100	15	600	79	9.8	91
6	730	1760	1760	3100	15	601	78	8.5	78
6	755	1760	1760	3100	15	601	78		
6	755	1800	1800	3600	15	601	78		
6	800	2500	2500	0	15	601	78		
6	810	1000	1000	0	15	406	78		
6	825	225	225	0	15	406	78		
6	835	300	300	0	15	367	78		
6	853	75	75	0	15	308	78		
6	910	25	25	0	15	275	78		
6	1040	25	25	0	15	187	78		
6	1130	0	0	0	15	105	78		
6	1300	0	0	0	15	78	78		
6	1300	0	0	0	0	0	0	0.0	0
1	1450	0	0	0	15	0	76	28.5 *	0
1	1525	500	500	500	15	70	76		
2	720	500	500	500	15	70	76		
2	725	1760	1760	2000	15	70	76		
2	728	1760	1760	3100	15	70	76		
2	730	1760	1760	3100	15	70	76		
2	815	1760	1760	3100	15	131	76		
2	1025	1760	1760	3100	15	131	75	28.3	84
3	740	1760	1760	3100	15	131	78	27.3	68
4	742	1760	1760	2950	15	125	78	27.0	63
4	1040	1760	1760	3100	15	125	78		
7	745	1760	1730	2825	15	128	76	25.3	76
7	810	1760	1760	2925	15	128	76		
8	750	1760	1760	2700	15	129	74	24.8	63
9	745	1760	1760	2520	15	74	24	23.3	79
9	805	1760	1760	2520	15	129	24		
9	915	1760	1760	3100	15	255	74		
9	1335	1760	1760	3100	15	598	74		
9	1400	1760	1760	3100	15	599	77	23.5	85
0	740	1760	1760	3100	15	598	74	22.5	112
1	750	1760	1760	3100	15	598	76	21.3	110
4	740	1760	1760	3150	15	598	74	17.3	110
5	725	1760	1760	3150	15	597	73	16.0	120
5	732	1760	1760	3150	15	597	69	14.5	115 *
7	739	1760	1760	3150	15	597	70	13.0	112
3	745	1760	1760	3150	15	597	71	11.8	111
1	735	1760	1760	3150	15	604	72	7.5	106

NOTE: * INDICATES MUT OR EFFLUENT SAMPLE TAKEN

REMARKS:

- 1) BELLOWS FAILURE
- MUT REFILL (50L)
- BELLOWS NITROGEN SUPPLY LOW
- BELLOWS NITROGEN SUPPLY RESTORED

TABLE 10-11
OPERATING PARAMETERS FOR TEST LOOP 2

AUTOCLAVE #29 THI LEAD TEST #2
FEBRUARY 1983

DAY	TIME	P _s PSI	P _a PSI	P _b PSI	P _{mut} PSI	AC T F	MUT T F	MUT LEVEL INCHES	EFFLUENT FLOW ml/hr
								6.3	102
1	748	1760	1760	3150	15	603	75		
1	1305	1760	1760	3150	15	599	71	28.4 *	120
2	755	1760	1760	3150	15	600	76	27.4	92
3	750	1760	1760	3150	15	600	79	26.0	94
4	805	1760	1760	3150	15	600	78	24.8	102 *
7	735	1760	1760	3150	15	600	81	21.1	122
8	740	1760	1760	3150	15	599	83	19.3	98 *
9	740	1760	1760	3150	15	600	84	18.5	111 *
10	743	1760	1760	3150	15	599	83	17.3	108
11	800	1760	1760	3150	15	599	83	15.8	105
14	745	1760	1760	3150	15	597	81	11.5	133
15	730	1760	1760	3150	15	596	80	10.3	112
16	730	1760	1760	3150	15	597	80	8.8	115
16	1530	1760	1760	0	15	83	80	8.3	115
16	2030	1760	1760	0	5	83	80	8.0	115
17	735	1760	1760	0	10	74	75	8.0	89 *
17	735	1760	1760	0	10	78	76	8.0	77
18	728	1760	1760	0	10	78	76	8.0	77
18	740	0	0	0	0	0	0	0.0 *	0
18	740	0	0	0	0	0	0	0.0	0
27	1800	0	0	0	0	0	0	0.0	0
27	1800	0	0	0	0	0	0	0.0	0
27	2015	1760	1760	3150	15	75	75	21.8 *	160 *
27	2035	1760	1760	3150	15	150	74	21.5	160
28	735	1760	1760	3150	15	150	74	21.0	112 *
28	1930	1760	1760	3150	15	595	74	20.5	112

NOTE ** INDICATES MUT OR EFFLUENT SAMPLE TAKEN

COMMENTS:

DAY

- 1 MUT REFILLED (50 L.)
- 16 BELLOWS FAILURE
- 18 SHUT DOWN CYCLE #1 COMPLETE
- 22 START UP CYCLE #1

TABLE 10-12 OPERATING PARAMETERS FOR TEST LOOP 2

COCLAUSE #29 TMI LEAD TEST #2
 MCH 1983

TIME	P _a PSI	P _b PSI	P _b PSI	P _{mut} PSI	AC T F	MUT T F	MUT LEVEL INCHES	EFFLUENT F _i ml/hr
1000	1760	1760	3150	15	599	73	19.1	78
1910	1760	1760	3150	15	599	73		
2010	1760	1760	3150	15	503	73		
750	1750	1750	3100	15	500	74	17.3	112
1900	1750	1750	3100	15	501	74		
2045	1750	1750	3100	15	597	74		
822	1760	1760	3150	15	601	74	15.1	63
1900	1760	1760	3150	15	601	74		
2000	1760	1760	3150	15	505	74		
950	1760	1760	3150	15	501	76	13.3	72
1910	1760	1760	3150	15	500	76		
2040	1760	1760	3150	15	597	76		
640	1760	1760	3150	15	601	77	12.1	120
1900	1760	1760	3150	15	600	77		
2000	1760	1760	3150	15	504	77		
630	1760	1760	3150	15	500	75	10.5	109
1910	1760	1760	3150	15	499	75		
2110	1760	1760	3150	15	595	75		
730	1760	1760	3150	15	601	80	9.0	97
2150	1760	1760	3150	15	601	80		
2250	1760	1760	3150	15	505	80		
2100	1760	1760	3150	15	501	77	28.9 *	120
2210	1760	1760	3150	15	595	77		
910	1760	1760	3150	15	600	79	28.5	81 *
2000	1760	1760	3150	15	601	79		
2100	1760	1760	3150	15	505	79		
745	1760	1760	3125	15	502	78	27.0	92
1940	1760	1760	3125	15	503	78		
2055	1760	1760	3125	15	597	78		
825	1760	1760	3150	15	598	80	25.9	95
1310	1760	1760	3150	15	598	78	22.0	65
1155	1760	1760	3150	15	597	77	21.1	98
1315	1760	1760	3125	15	600	77	19.9	95
812	1760	1760	3125	15	599	77	19.0	94
805	1760	1760	3125	15	600	81	17.9	90
815	1760	1760	3125	15	599	78	14.6	95
800	1760	1760	3125	15	599	79	13.5	94
750	1760	1760	3125	15	599	81	12.3	76 *
800	1760	1760	3125	15	598	79	11.0	96
830	1760	1760	4195	15	598	79		
1500	1760	1760	4195	15	135	79		
1510	1760	1760	3150	15	135	79		
810	1750	1750	3125	15	132	77	6.0 *	165
800	1760	1760	3125	15	131	79	30.0	117
800	1760	1760	3125	15	132	78	28.5	120
810	1760	1760	3125	15	131	73	26.8	120
830	1760	1760	3150	15	131	73	25.4	120
915	1760	1760	3150	15	132	73		
1520	1760	1760	3150	15	595	73		

TE "*" INDICATES MUT OR EFFLUENT SAMPLE TAKEN

MENTS;
 Y

TABLE 10-13

OPERATING PARAMETERS FOR TEST LOOP 2

TOCLAVE#29 THI LEAD TEST #2
 RIL 1983

Time	Ps PSI	Pa PSI	Pb PSI	Pmut PSI	AC T F	MUT T F	MUT LEVEL INCHES	EFFLUENT F ml/hr
740	1760	1760	3150	15	598	73	19.6	117
740	1760	1760	3150	15	600	77	18.5	103
1200	1760	1760	3150	15	598	76	17.1	100 *
1300	1760	1760	3150	15	600	74	16.3	90
1700	1760	1760	3150	15	601	74	15.3	72
600	1760	1760	3150	15	599	75	10.9	113
740	1760	1760	3150	15	600	73	9.5	110
800	1760	1760	3150	15	600	77	6.8 *	124
910	1760	1760	3150	15	598	70	27.0	120
700	1760	1760	3150	15	597	70	22.5	116
800	1760	1760	3150	15	599	72	20.8	121
800	1760	1760	3150	15	599	72	19.5	123 *
800	1760	1760	3150	15	599	70	18.0	120
800	1760	1760	3150	15	599	76	15.0	123
800	1760	1760	3150	15	599	71	12.3	117
800	1760	1760	3150	15	599	76	11.7	124
700	1760	1760	3150	15	599	80	9.4	110
1000	1760	1760	3150	15	599	80		
1000	1760	1760	4200	15	588	80		
1020	1760	1760	4200	15	100	80		
1000	1760	1760	3150	5	100	80		
800	1760	1760	3150	5	100	77	6.0	136
0	0	0	0	0	0	0	0.0	0

e "X" INDICATES MUT OR EFFLUENT SAMPLE TAKEN

REMARKS:

REFILLED MUT

MUT N2 SPARGED - MUT 5 PSI AIR

TOCLAVE#29 THI LEAD TEST #2
 RIL 1983

TIME	Ps PSI	Pa PSI	Pb PSI	Pmut PSI	AC T F	MUT T F	MUT LEVEL INCHES	EFFLUENT F ml/hr
800	0	0	0	0	0	0	0.0	0
800	0	0	0	0	0	0		

NOTE ** INDICATES MUT OR EFFLUENT SAMPLE TAKEN

Table 10-14
 FRACTION OF SULFUR ATOMS STOPPED WITHIN A 10 NM SLICE OF
 MATERIAL AT VARIOUS DEPTHS BELOW THE SURFACE

Depth of Center of Slice (nm)	Total Dose (S_2^+/cm^2)		
	5×10^{15}	1×10^{16}	5×10^{16}
5	0.175	0.131	0.190
15	0.149	0.131	0.216
25	0.162	0.145	0.206
35	0.162	0.154	0.165
45	0.129	0.142	0.110
55	0.088	0.115	0.056
65	0.058	0.072	0.029
75	0.032	0.047	0.014
85	0.019	0.034	0.007
95	0.013	0.020	0.003
105	0.006	0.007	0.001
115	0.006	0.003	0.001
Total	0.999	1.001	0.998

10.6 Auger and X-Ray Photoelectron Spectroscopy (XPS) Studies of Sulfur Pick-up by Archive OTSG Surfaces.

This Appendix section describes the detailed analytical methodology, including standards preparation, that was applied to OTSG surface analyses for sulfur pickup following exposure of archive tubing samples to a preconditioning at elevated temperature in simulated reactor coolant with H_3BO_3 , $LiOH$, and very dilute SO_4^{2-} anion.

Preparation of Standards

Six sections of unconditioned archive Inconel 600 OTSG tubing, approximately 1 cm x 1 cm on the sides, were ground and polished on the ID side to provide a flat surface for mounting on a heat sink.

The standards were prepared by exposing the OD surfaces of the ground specimens to 150 KeV S_2^+ -ions to various doses ranging from 5×10^{15} S_2^+ -ions/cm² to 5×10^{16} S_2^+ /cm². Theoretical calculations predict a mean penetration depth of 320 Å with a straggling of 130 Å, so that 99 percent of the ions would be stopped within 710 Å from the entry surface.

Analysis of Standards

Figure 10-16 shows the AES analyses of three standards (5×10^{15} S_2^+ /cm², 1×10^{16} S_2^+ /cm², 5×10^{16} S_2^+ /cm²) to a depth of ~1200 Å. The vertical scale represents normalized peak-to-peak heights of the sulfur signal (n_s), calculated as follows:

$$n_s = (h_s/\alpha_s) / \left(\sum_i h_i/\alpha_i \right) \quad (10.4-1)$$

where h_s is the peak-to-peak height of the sulfur line in the derivative spectrum

α_s is the sensitivity factor as defined in Reference 16.

h_i , α_i are analogous quantities for element i and the summation is over all elements detected (S, C, O, Cr, Fe, Ni, Ti).

The horizontal scale represent a depth below the surface, based on a known sputtering rate of 50 Å/min (Reference 17).

For each curve in Figure 10-16, the fractional area of a 10 nm slice was compared with the total area under the curve. The total area under the curve represents a known quantity of sulfur and the fractional areas are proportional to the fraction of sulfur atoms stopped within each slice. Table 10-14 summarizes the results of the calculation.

The concentration of S in each slice is calculated from the formula

$$x_s = 2f\phi t / (N + 2f\phi t) \quad (10.4-2)$$

where ϕt = ion fluence (ions/cm²) or total dose

f = fraction of ions stopped within the selected slice (Table 1)

N = number of non-sulfur atoms within the slice (estimated at 9×10^{16} atoms, based on pure nickel)

By plotting normalized peak-to-peak heights (Equation 10.4-1) vs. sulfur concentrations (Equation 10.4-2), a calibration curve for sulfur analysis is obtained (Figure 10-17). The calibration curve of Figure 10-17 is based on the data obtained from the standards with 5×10^{15} and 1×10^{16} ions/cm². The data for the third standard need to be corrected for sulfur loss due to sputtering during ion implantation, an effect that can be neglected for the lower fluences.

Determination of Detection Limits

When the sulfur peak-to-peak height becomes less than twice the noise level in the derivative Auger spectrum, the apparent sulfur concentration may be 100 percent in error and that concentration constitutes the instrumental detection limit. Lower concentrations will go undetected or will be determined with very low accuracy if detected. The instrumental detection limit for this investigation is encountered at the last point of each of the curves in Figure 10-16. From Table 10-14, the corresponding number of s atoms is calculated to be $0.006 \times 5 \times 10^{15} \times 2 = 6 \times 10^{13}$ atoms in a 10 nm slice.

This is converted to $\mu\text{g}/\text{cm}^2$ by multiplying the number of atoms by the mass of a sulfur atom ($1.66 \times 10^{-27} \text{ kg} \times 32$). The result is a detection limit of $3 \times 10^{-3} \mu\text{g}/\text{cm}^2$ in a 10 nm slice.

The detection limit for sulfur in the XPS technique was determined as the sulfur level at which the uncertainty in the sulfur peak minus background value was as great as the scatter of the points in the background. It was found to be five times the Auger detection limit, or $15 \times 10^{-3} \mu\text{g}/\text{cm}^2$ in a 10 nm slice.

Analysis of Conditioned Samples

Six areas were analyzed on Inconel 600 samples cut from TMI-1 OTSG tubes which had been subjected to elevated temperature conditioning in simulated reactor coolant chemistry. No sulfur was detected in any of the specimens at any depth level, but all areas showed significant boron levels. The boron signal in the Auger spectrum consisted of two peaks, the main peak at 170 eV and a secondary peak at 152 eV. The peak-to-peak height of the secondary peak was about half that of the main peak. Normal boron signals consist of only one peak at 179 eV. The reason for the shift and the appearance of a second peak is not clear at this time. One possibility is that a boron-compound was formed, but the compound has not been identified.

Because of the proximity of the second boron peak and the sulfur signal, X-ray photoelectron spectroscopy (XPS) was used to differentiate between sulfur and boron. The XPS boron signal consisted of a single line indicating a 1s binding energy of 190.9 eV. No sulfur was detected by XPS. This limits the amount of sulfur that might have been present to $0.15 \mu\text{g}/\text{cm}^2$ in the first 100 nm below the surface and to one tenth of that amount within the first 10 nm below the surface.

The Auger analyses are summarized in "composition tables" attached to the report. The compositions given are essentially normalized peak-to-peak heights (similar to Equation 10.4-1, for each element) and not calibrated.

They give, however, some qualitative idea of how the composition changes with sputtering time. The sputter rate used was 5 nm/min.

Summary

Calibration curves for AES analysis of sulfur in Inconel 600 are available. Unfortunately, the presence of an unidentified boron compound makes the use of AES on the GPU-N tubes undesirable, at least for sulfur analysis. XPS is less sensitive to sulfur, but can be used to differentiate between boron and sulfur. The detection limit for sulfur (by XPS) has been determined. Standards are available to calibrate the XPS technique for quantitative sulfur analysis. (However, the calibration is costly and time consuming.)

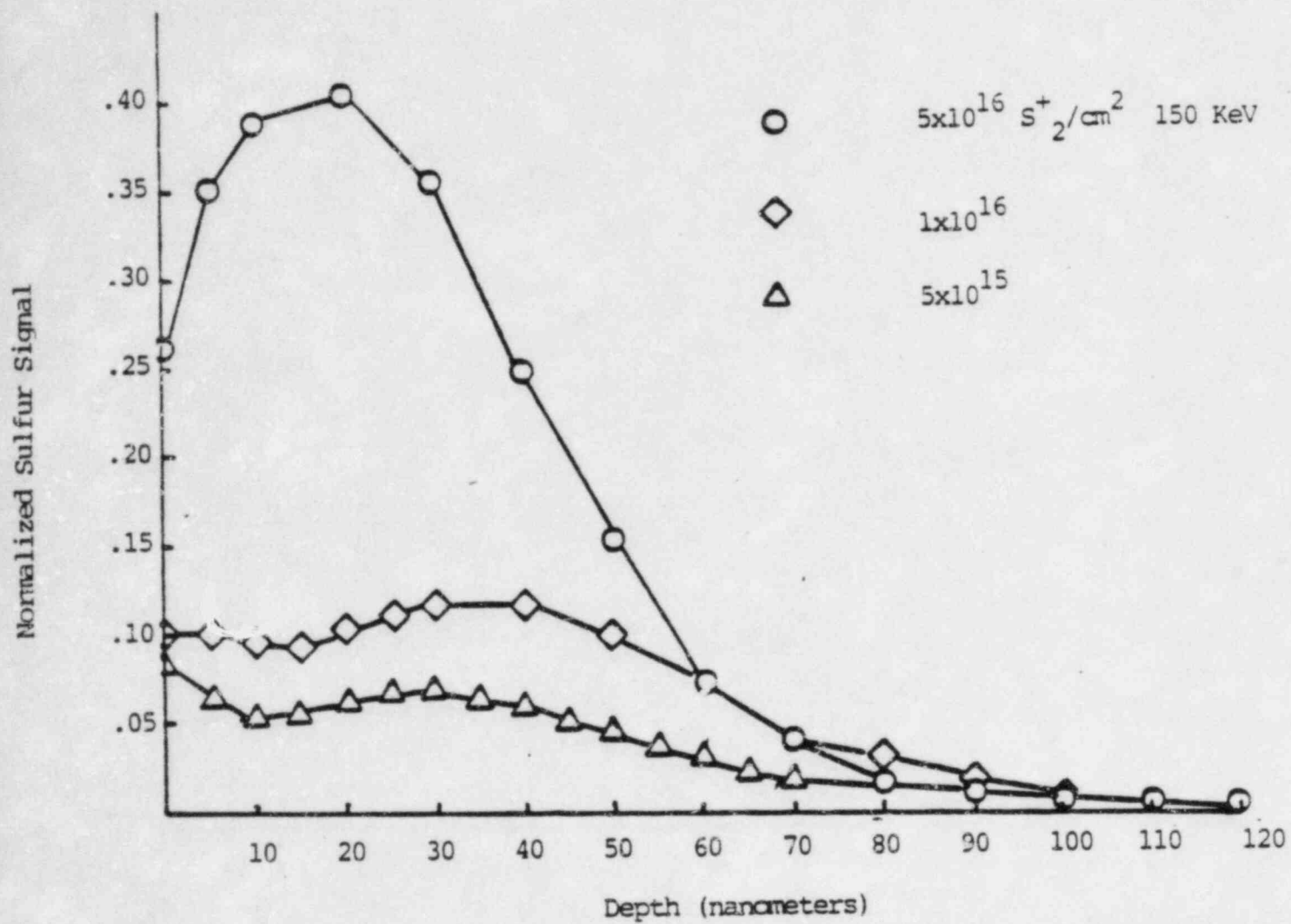


Fig. 10-16 Normalized Sulfur peak-to-peak height versus depth below the surface for three ion-implanted standards

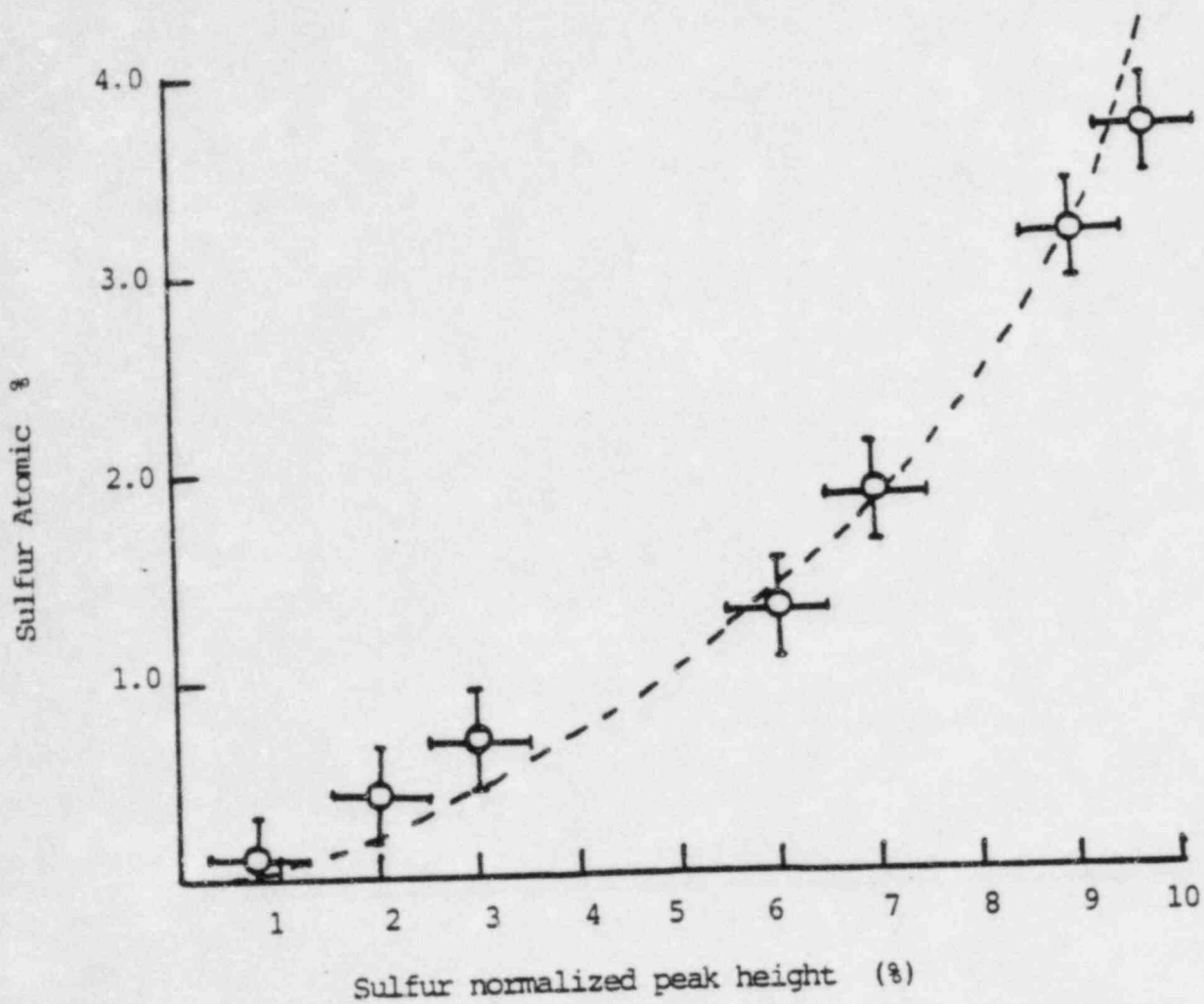


Fig. 10-17 Calibration Curve for Sulfur Analysis in Inconel Alloy 600 by AES.

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